OCTOBER-DECEMBER • 1954

VOLUME XXVII • NUMBER FOUR

RUBBER CHEMISTRY AND TECHNOLOGY

PUBLISHED QUARTERLY BY THE
DIVISION OF RUBBER CHEMISTRY
OF THE AMERICAN CHEMICAL SOCIETY

KOSMOS 60 RF
KOSMOS 60 RF

KOSMOS 60 RF
KOSMOS 60 RF

Kosmos 60 is today the most talked about furnace black for reinforcing natural and synthetic rubber. It originates from oil and is perfected by United's exclusive process. Its superb processing and balance of strength make for the best in rubber products.

UNITED CARBON COMPANY, INC.

CHARLESTON 27, W. VA.

NEW YORK • AKRON • CHICAGO • BOSTON

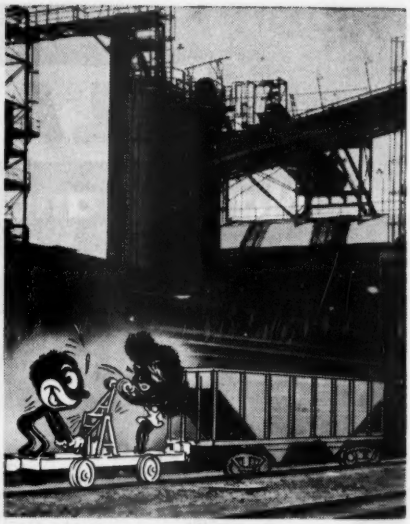
CANADA: CANADIAN INDUSTRIES LIMITED

Shipping Philblack*

Phillips modern handling and shipping techniques make certain that Philblack arrives at your shipping dock in excellent condition. Specially designed hopper cars cut customers' unloading time as much as 30%. New, flat, shaped bags stack like bricks . . . take up 25% less space in trucks and warehouses.

For expert advice on your carbon black problems, consult your Philblack technical representative.

*A Trademark.



Philblack hopper cars are carefully guarded from moisture penetration during loading operations.

Know the Philblacks!

KNOW WHAT THEY'LL DO FOR YOU!

A — **Philblack A, FEF Fast Extrusion Furnace**
Ideal for smooth tubing, accurate molding, satiny finish. Mixes easily. High, hot tensile. Disperses heat. Non-staining.

I — **Philblack I, ISAF Intermediate Super Abrasion Furnace**
Superior abrasion resistance at moderate cost. Very high resistance to cuts and cracks. More tread miles at high speeds.

O — **Philblack O, HAF High Abrasion Furnace**
For long, durable life. Good electrical conductivity. Excellent flex. Fine dispersion.

E — **Philblack E, SAF Super Abrasion Furnace**
Toughest black on the market. Extreme abrasion resistance. Withstands aging, cracking, cutting and chipping.

Phillips 66

PHILLIPS CHEMICAL COMPANY, Philblack Sales, 318 Water Street, Akron 8, Ohio. Export Sales: 80 Broadway, New York 5, N. Y. West Coast: Harwick Standard Chemical Company, Los Angeles, Calif. Canada: H. L. Blachford, Ltd., Montreal and Toronto.

Entered as second-class matter March 19, 1943, at the Post Office at Lancaster, Pa., under the Act of August 24, 1912. Acceptance for mailing at special rate of postage provided for in paragraph (d-2), Section 34.40, P. L. and R. of 1948, authorized September 25, 1940.

Witco BLACKS for Natural and Chemical Rubbers

...over thirty years of research and dependable quality production

CHANNEL BLACKS

Continental AA—Witco No. 12—Easy Processing (EPC)
Continental A—Witco No. 1—Medium Processing (MPC)
Continental F—Witco No. 6—Hard Processing (HPC)
Continental R-40—Conducting (CC)

FURNACE BLACKS

Continex® SRF—Natural Gas Type, Semi-Reinforcing
Continex SRF-NS—Natural Gas Type, Semi-Reinforcing —Non-Staining
Continex HMF—Natural Gas Type, High Modulus
Continex HAF—Oil Type, High Abrasion
Continex FEF—Oil Type, Fast Extruding

Whatever your requirements, rely on Witco-Continental as your source of dependable quality carbon black products. For complete information, and assistance with your problems, consult Witco's Technical Service Laboratory.

WITCO

WITCO CHEMICAL COMPANY
CONTINENTAL CARBON COMPANY
260 Madison Avenue, New York 16, N. Y.

Amarillo · Akron · Boston · Chicago · Houston · Cleveland
San Francisco · Los Angeles · London and Manchester, England

TIME-TESTED VERSATILE

SHARPLES ACCELERATOR

SA 52

TETRAMETHYL-THIURAM DISULFIDE

Natural Rubber **Nitrile Rubber** **GR-S**	For HEAT RESISTANCE—SUPER AGING—TARNISH RESISTANCE Use 3.0-4.0 PHR of **SA 52** as the VULCANIZING AGENT. For FAST, TIGHT CURE Use 0.4-1.5 PHR of **SA 52** as PRIMARY ACCELERATOR with 1.0-2.5 PHR of sulfur. To ACTIVATE THIAZOLES Use 0.05-0.30 PHR of **SA 52** as a SECONDARY ACCELERATOR.
Butyl Rubber	For STANDARD ACCELERATION Use 1.0-3.0 PHR of **SA 52** with 0.5-2.0 PHR of sulfur. For HEAT RESISTANCE—TARNISH RESISTANCE Use 3.0-4.0 PHR of **SA 52** as the VULCANIZING AGENT.
Neoprene GN	To INCREASE SCORCH TIME Use 1.0-2.0 of **SA 52**.

SHARPLES TRADE MARK CHEMICALS

SHARPLES CHEMICALS INC.

West Coast: Los Angeles · Berkeley · Portland · Tacoma
Shawinigan Chemicals Ltd., Montreal · Toronto
Arco Company International, New York

Thiokol®

PLASTICIZER TP-90 B

Yields Maximum Low Temperature Flexibility and Maintains Excellent Physical Properties

"Thiokol" Plasticizer TP-90 B is an efficient low temperature plasticizer. Even at high concentrations it does not appreciably impair the physical properties of the compounds in which it is used.

"Thiokol" Plasticizer TP-90 B is highly compatible with natural rubber, Neoprene, nitrile-type rubbers and GR-S. It imparts excellent low temperature flexibility to these elastomers and maintains high resilience over a wide temperature range.

The following results illustrate how "Thiokol" TP-90 B yields excellent low temperature flexibilities while still maintaining the physical properties:

	Natural Rubber	Neoprene GN	Hycar OR-15	Paracril-B	GR-S
TP-90B, p. h. r.	30	20	30	30	30
Cure, min. /° F.	30/310	45/300	30/310	30/310	30/310
Tensile, p. s. i.	2200	2600	2380	2250	1500
Elongation, %	530	410	300	350	380
Shore Durometer	42	68	70	61	45
Low Temperature Flexibility**	**–95°F**	**–70°F**	**–70°F**	**–80°F**	**–95°F**

**Determined according to a modification of ASTM method D 1043-49T. The temperatures shown are the values at which the absolute torsional moduli are 10,000 p. s. i. Although the specimens were still quite flexible, G10,000 was arbitrarily chosen as the stiffening point.

For technical information and samples, write:

This information is believed to be accurate. However, no warranty is expressed or implied regarding the accuracy of these data, or the use of this product.

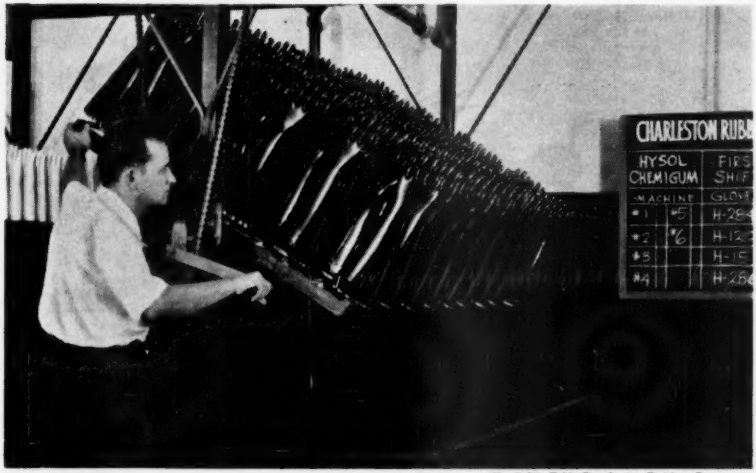
Thiokol Chemical Corporation

SYNTHETIC RUBBERS • PLASTICIZERS • CHEMICALS • SOLID PROPELLANTS

784 NORTH CLINTON AVENUE, TRENTON 7, NEW JERSEY

In Canada: Naugatuck Chemicals Division, Dominion Rubber Company, Elmira, Ontario

HELPING HANDS for chemical workers that stay on the job longer are these heavy-duty gloves of CHEMIGUM—the easy-processing nitrile rubber. They are made by multiple dipping the solution of rubber cement onto the porcelain forms. Photo courtesy Charleston Rubber Company, Charleston, S. C.



"Hy-Sol"—T.M. Charleston Rubber Company

BETTER GLOVES—BETTER PROFITS

with easier-processing CHEMIGUM

RUBBER gloves for chemical workers often have been a problem to their manufacturers. Ordinary rubbers cannot withstand the deteriorating effects of a number of chemicals, particularly oils, solvents and alkalies. Those few that can, usually are difficult to process.

Solution to the problem for one glove-maker came in the form of a solution of CHEMIGUM—the butadiene-acrylonitrile copolymer noted for its ease of processing and outstanding physical properties. This user found CHEMIGUM gave him faster, more uniform "breakdowns" on the mill and excellent solubility characteristics, *plus* resulting in a glove of superior chemical resistance and general durability.

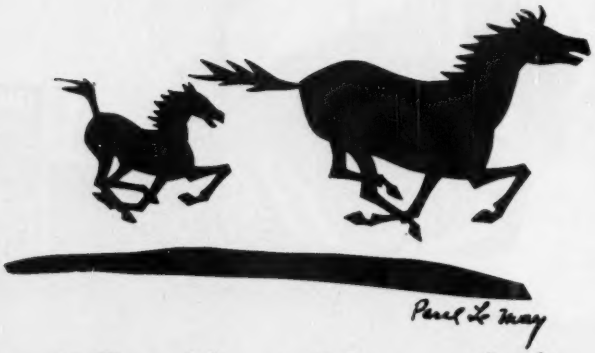
Its use in gloves is another example of how smaller-baled, lighter-colored, easier-processing CHEMIGUM is helping many manufacturers to produce better, oil-resistant rubber products faster and more profitably. Details on how CHEMIGUM can help you are available from the greatest producer of synthetic rubbers and related resins by writing to:

Goodyear, Chemical Division,
Akron 16, Ohio

CHEMICAL GOODYEAR DIVISION

Chemigum, Pliobond, Pliolite, Plio-Tuf, Pliovic—T. M.'s The Goodyear Tire & Rubber Company, Akron, Ohio

Use-Proved Products — CHEMIGUM · PLIOBOND · PLIOLITE · PLIO-TUF · PLIOVIC · WING-CHEMICALS—The Finest Chemicals for Industry



..."feeling his oats"

We are feeling our oats because of the enthusiastic acceptance of ***TEXAS 109,*** the new black which gives the compounder these plus features at HAF prices.

FAST CURE—Ph 9 plus

ULTIMATE TENSILE—Superior to channel black in both natural and GR-S

ELONGATION—Superior to channel black in both natural and GR-S

CRACKING—Equivalent to HAF in GR-S

ABRASION—Equivalent to ISAF in LTP and GR-S

. . . All this at HAF prices . . .

Write, wire or telephone for samples and information.

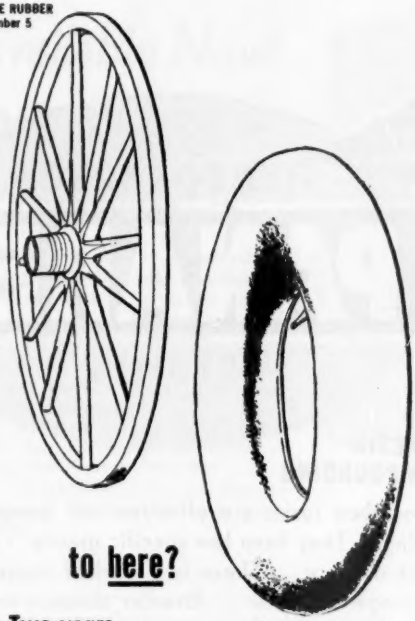
TEXAS CHANNEL BLACKS ®

Sid Richardson
CARBON CO.
FORT WORTH, TEXAS

GENERAL SALES OFFICES
EVANS SAVINGS AND LOAN BUILDING
AKRON 8, OHIO

THE HISTORY OF THE RUBBER INDUSTRY— Number 5

how long did it take to get from here to here?



Answer: Two years.

The principle of an inner tube is simple, and of such ancient application that it could not be patented.

Inner tubes, as we think of them today, were probably used about 1890. By 1892—two years later—they were being used widely, and beginning to appear as the detachable tube, for double tube tires, and the vulcanized-in type, used in single tube tires.

Two Monsanto accelerators, Thiofide (powder) and Thiofide S (seeds), can be used successfully in a wide variety of stocks. The seeds give maximum speed and completeness of dispersion. For more information about these accelerators and other products, see catalog "Monsanto Chemicals for the Rubber Industry." If you do not have a copy, write to MONSANTO CHEMICAL COMPANY, Rubber Service Department, 920 Brown Street, Akron 11, Ohio.

Monsanto Chemicals For the Rubber Industry

ANTIOXIDANTS
Flectol* H
Santoflex* B
Santoflex BX
Santoflex 35
Santoflex AW
Santowhite* Crystals
Santowhite MK
Santowhite L

ALDEHYDE AMINE ACCELERATORS
A-32
A-100

MERCAPTO ACCELERATORS
Santocure*
El-Sixty*
Mertax (Purified Thiotax)
Thiotax (2-Mercapto benzothiazole)
Thiofide* (2,2' dithio-bis benzothiazole)

GUANIDINE ACCELERATORS
Diphenylguanidine (D.P.G.)
Guantal*

ULTRA ACCELERATORS FOR LATEX, ETC.
R-2 Crystals
RZ-50
RZ-50-B
Pip-Pip
Thiurad* (Tetramethylthiuram disulfide)
Ethyl Thiurad (Tetraethylthiuram disulfide)
Mono Thiurad (Tetramethylthiuram monosulfide)
Methasan* (Zinc salt of dimethyl dithiocarbamic acid)
Ethasan* (Zinc salt of diethyl dithiocarbamic acid)
Butasan* (Zinc salt of dibutyl dithiocarbamic acid)

SPECIAL MATERIALS
Thiocarbanilide ("A-1")
Santovar*-A
Santovar-O
Sulfasan R
Insoluble Sulfur "60"

COLORS

REODORANTS

*Reg. U. S. Pat. Off.

MONSANTO CHEMICALS—PLASTICS

SERVING INDUSTRY... WHICH SERVES MANKIND

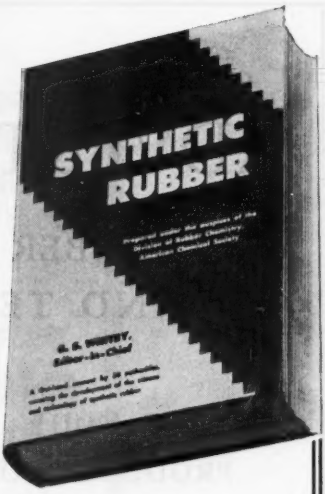
Look at...
HYDROCARBON
PANAREZ
RESINS
AS A
QUALITY
ECONOMICAL RESIN
IN RUBBER COMPOUNDING
PANAREZ hydrocarbon resins are effective and inexpensive for rubber compounding. They have low specific gravity · Low odor · Show no effect on cure · There is a marked improvement in processing · Longer flex life · Greater abrasion resistance · Better color stability · Electrical characteristics are excellent.
Prompt shipments made in carload or single drum quantities. Write for samples.

	Color Gardner	Softening Point, °F	Specific Gravity	Acid Number
PANAREZ 3-210	9	200-220	1.049	0-1
PANAREZ 6-210	11	200-220	1.106	0-1
PANAREZ 12-210	16	200-220	1.054	0-1

PAN AMERICAN CHEMICALS
PAN AMERICAN DIVISION
Pan American Refining Corp.
122 EAST 42ND STREET · NEW YORK 17, N. Y.
PAN AMERICAN *Chemicals*

Available Now!

SYNTHETIC RUBBER



A first-hand account by 38 authorities, covering the development of the science and technology of synthetic rubber

The Editorial Board

G. S. WHITBY, Professor of Rubber Chemistry and Director of Rubber Research, *University of Akron*

C. C. DAVIS, Chief Chemist, *Boston Woven Hose and Rubber Co.*; Editor of *Rubber Chemistry and Technology*

R. F. DUNBROOK, Assistant Director of Research, *Firestone Tire and Rubber Company*

THIS is the first exhaustive and authoritative account of the subject of synthetic rubber. Prepared under the auspices of the Division of Rubber Chemistry of the American Chemical Society, the book records the research and development that made possible the production of synthetic rubber in quantity in the U. S. and Canada during World War II. It shows how the growth from a mere 2500 tons in 1941 to a peak of 900,000 tons ten years later was achieved. The book examines the manufacture of the necessary raw materials, their conversion into synthetic rubber, and the industrial utilization of the product. It also reviews the great volume of research which has been carried out in the United States since the war—covering all the phases of the chemistry and physical chemistry of synthetic rubber.

As a comprehensive account of both the scientific and practical aspects of the subject, this volume fulfills a real need in the literature of synthetic rubber.

1954 1044 pages Illustrated $18.00

Send for your ON-APPROVAL copy today

JOHN WILEY & SONS, Inc.

440 Fourth Avenue New York 16, N. Y.

ADVERTISE *in*

RUBBER CHEMISTRY AND TECHNOLOGY

KEEP YOUR NAME AND YOUR PRODUCTS CONSTANTLY BEFORE THE RUBBER TECHNOLOGIST

Advertising rates and information about available locations may be obtained from E. H. Krismann, Advertising Manager, Rubber Chemistry and Technology, care of E. I. du Pont de Nemours & Company, 40 East Buchtel Ave. at S. High St., Akron 8, Ohio.

CABOT AS THE WORLD'S ONLY CARBON BLACK MANUFACTURER OF CHANNEL, FURNACE AND THERMAL GRADES

offers the greatest variety of

NON-STAINING CARBON BLACKS

available to the rubber industry

CABOT'S NON-STAINING CARBON BLACKS		
STERLING SO	FEF	Fast Extruding Furnace
STERLING V Non-Staining	GPF	General Purpose Furnace
STERLING NS	SRF	Semi-Reinforcing Furnace
PELLETEX NS	SRF	Semi-Reinforcing Furnace
STERLING MT Non-Staining	MT	Medium Thermal

AND, although Vulcan 3 HAF (High Abrasion Furnace), Vulcan 6 ISAF (Intermediate Super Abrasion Furnace), and Vulcan 9 SAF (Super-Abrasion Furnace) carbon blacks made from oil are used primarily for their high reinforcement properties, they also possess non-staining characteristics.

GODFREY L. CABOT, INC.
77 FRANKLIN ST., BOSTON 10, MASS.

CABOT

chemicals for the rubber industry

ACCELERATORS

Thiazole

MBT (Mercaptobenzothiazole)
MBT-XXX (Specially Refined—Odorless)
MBTS (Benzothiazyldisulfide)
NOBS* No. 1 Accelerator
NOBS* SPECIAL Accelerator

Guanidine

DPG (Diphenylguanidine)
DOTG (Diorthotolylguanidine)
Accelerator 49

ANTIOXIDANT

Antioxidant 2246*
(Non-staining, non-discoloring type)

PEPTIZER

Pepton® 22 Plasticizer

RETARDER

Retarder P.D.

SULFUR

Rubber Makers' Grade

*Trade-mark

AMERICAN Cyanamid COMPANY Calco®

INTERMEDIATE & RUBBER CHEMICALS DEPARTMENT
BOUND BROOK, NEW JERSEY, U.S.A.

SALES REPRESENTATIVES AND WAREHOUSE STOCKS: Akron Chemical Company, Akron, Ohio • Ernest Jacoby and Company, Boston, Mass. • Herron & Meyer of Chicago, Chicago, Ill. • H. M. Royal, Inc., Los Angeles, Calif. • H. M. Royal, Inc., Trenton, N. J. • In Canada: St. Lawrence Chemical Company, Ltd., Montreal and Toronto

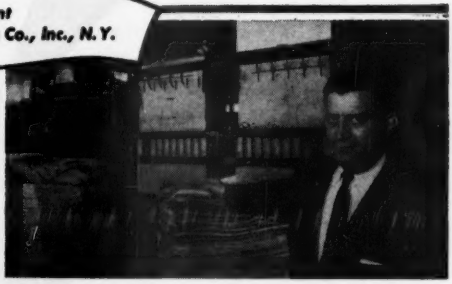
"Today's tire manufacturers are using bonding agents* that literally *weld* the cords to the rubber"

says C. H. Peterson, President U. S. Rubber Reclaiming Co., Inc., N. Y.

"THIS positive bonding has caused us one headache after another," adds Mr. Peterson. "The *better* the bond between the rubber and the tire fabric, the *tougher* our job becomes."

U.S. Rubber Reclaiming Co., Inc., has been forced to redesign its separation system time and again to cope with the constantly improved tires. Better grinding equipment has had to be developed to tear the stubborn fabric from the rubber. The power of the grinders, which was originally 150 h.p., has been increased steadily until it is now up to 450 h.p.

Although a "headache" to the U.S. Rubber Reclaiming Co., Inc., the toughness of today's tires is a definite advantage to the motorist.



Mr. Peterson standing in front of the massive reclaiming equipment at the U. S. Rubber Reclaiming Co., Inc., plant in Cheektowaga, New York. At the left is a bale of reclaimed tire fabric, and at the right a pallet load of reclaimed rubber.

The rolling mill, commonly known as the "cracker." These powerful rolls actually tear the tires to pieces.

* A good deal of the credit for permanent rubber-fiber bonds in tires can be claimed by Koppers Resorcinol. Resins made from resorcinol form an excellent bond—one that will take repeated pounding and wear, will withstand prolonged flexure under grueling service conditions without separating. Because of their superb adhesive properties, resins made from Koppers Resorcinol have also found wide application in the manufacture of industrial belting, hose, and many other heavy-duty rubber products where a powerful, lasting bond is needed between reinforcing fibers and synthetic or natural rubber.

For further information, write to:

KOPPERS COMPANY, INC.

CHEMICAL DIVISION, DEPT. RCT-124 PITTSBURGH 19, PENNSYLVANIA

KOPPERS®

Koppers Resorcinol

SALES OFFICES: NEW YORK · BOSTON · PHILADELPHIA
ATLANTA · CHICAGO · DETROIT · LOS ANGELES

the only rubber plant that can't use

NEVILLE CHEMICALS

For all the others Neville has a complete line of Coumarone-Indene Resins, as well as Petroleum Resins, Reclaiming Oils, Softeners, and Plasticizers.

Speaking of plants, our main one is located in the Industrial East with another in fast-growing Southern California. We are branching out too with warehouses in South Kearny, N.J., Philadelphia, Los Angeles, Montreal, Toronto, and Boston. So, whether you are on the main stem or not, Neville Products are near you.

B-53

NEVILLE

NEVILLE CHEMICAL CO.

PITTSBURGH 25, PA.

Plants at Neville Island, Pa. and Anaheim, Cal.

Looking for
the finest in...

Rubber Chemicals?

PROCESS
ACCELERATE
PROTECT

NAUGATUCK offers a complete line of proven accelerators, activators, anti-oxidants, and special chemicals to give you thorough control of rubber product manufacture and performance.

†these products furnished either in powder form or fast-dispersing, free-flowing NAUGETS.

ACCELERATORS

THIAZOLES—
M-B-T | O-X-A-F
M-B-T-S

THIURAMS—
MONEX*† | TUEX†
MORFEX | ETHYL TUEX†
PENTEX*

DITHIOCARBAMATES—
ARAZATE* | ETHAZATE*†
BUTAZATE* | METHAZATE*†

ALDEHYDE AMINES—
BEUTENE* | HEPTEEN BASE*
TRIMENE* | TRIMENE BASE*

XANTHATES—
C-P-B* · Z-B-X*

ACTIVATORS

VULKLOR | DIBENZO G-M-F
D-B-A | G-M-F

ANTIOXIDANTS

AMINOX* | B-L-E*
ARANOX* | B-X-A
V-G-B* | FLEXAMINE
OCTAMINE* | BETANOX* Special

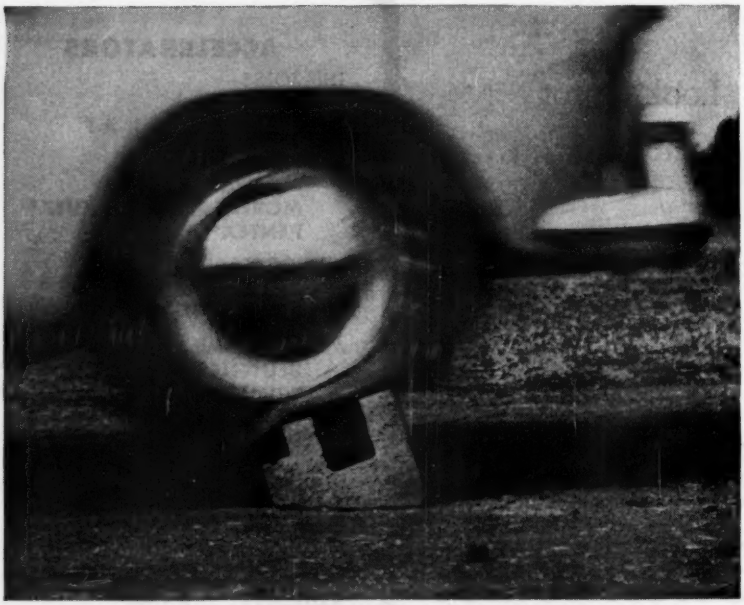
SPECIAL PRODUCTS

BWH-1 | SUNPROOF* Improved
CELOGEN | SUNPROOF* Junior
CELOGEN-AZ | SUNPROOF*—713
E-S-E-N | SUNPROOF* Regular
LAUREX* | SUNPROOF* Super
TONOX* | KRALAC* A-EP

SPECIAL PRODUCTS FOR SYNTHETIC POLYMERS
THIOSTOP K & N—short stops
POLYGARD—stabilizer

*Reg. U. S. Pat. Off.

Naugatuck Chemical
Division of UNITED STATES RUBBER COMPANY
341 Elm St., Naugatuck, Conn.
IN CANADA: NAUGATUCK CHEMICALS DIVISION
Dominion Rubber Company, Limited, Elmira, Ontario
Rubber Chemicals • Synthetic Rubber • Plastics • Agricultural Chemicals
Reclaimed Rubber • Latices



CIRCOSOL-2XH GIVES YOUR TIRES THE EXTRA SAFETY CUSTOMERS WANT

Circosol-2XH is the elasticator that gives you the tougher, more resilient rubber needed to make safer tires. And it does it without jacking costs sky high. Enough Circosol-2XH for an 8.00 x 15 size 100 level tire costs less than 2¢ more than the cheapest softener you can buy.

Tires made with Circosol-2XH have greater resistance to abrasion, and can take sharper impacts and a rougher all around beating than tires made with cheap softeners. Circosol-2XH helps inhibit the spread of cuts and helps tires go through hard driving on hot summer roads without damaging heat build-up.

You can get the full story on the advantages of Circosol-2XH from your local Sun Oil Company Representative—or write Department RC-10.

INDUSTRIAL PRODUCTS DEPARTMENT

SUN OIL COMPANY

SUNOCO®

PHILADELPHIA 3, PA. • SUN OIL COMPANY LTD., TORONTO & MONTREAL

Refiners of famous High-Test Blue Sunoco Gasoline

OCTOBER-DECEMBER • 1954

VOLUME XXVII • NUMBER FOUR

RUBBER CHEMISTRY AND TECHNOLOGY

PUBLISHED QUARTERLY BY THE
DIVISION OF RUBBER CHEMISTRY
OF THE AMERICAN CHEMICAL SOCIETY

CARBON BLACKS

for **RUBBER COMPOUNDING**

SAF (Super Abrasion Furnace)
STATEX®-125

HAF (High Abrasion Furnace)
STATEX-R

MPC (Medium Processing Channel)
STANDARD MICRONEX®

EPC (Easy Processing Channel)
MICRONEX W-6

FF (Fine Furnace)
STATEX-B

FEF (Fast Extruding Furnace)
STATEX-M

HMF (High Modulus Furnace)
STATEX-93

SRF (Semi-Reinforcing Furnace)
FURNEX®

• COLUMBIAN COLLOIDS •

COLUMBIAN CARBON CO. MANUFACTURER • **BINNEY & SMITH INC.** DISTRIBUTOR

500 TONS OF SMOKE A DAY

RUBBER CHEMISTRY AND TECHNOLOGY

Published Quarterly under the Auspices of the Division of Rubber Chemistry of the American Chemical Society,
Prince and Lemon Streets,
Lancaster, Pa.

Editor ..... C. C. DAVIS
Advertising Manager ..... E. H. KRISMANN
Secretary ..... A. M. NEAL
Treasurer ..... A. W. OAKLEAF

Vol. XXVII October-December, 1954 No. 4

CONTENTS

General Section PAGE

Officers iii
Spring Meeting of the Division of Rubber Chemistry, Louisville, Kentucky, April 14–16, 1954 iv
New Books and Other Publications v

Papers

Photoelastic Studies Concerned with Fatigue Phenomena in Rubber Articles. ATTILIO ANGIOLETTI 839
Dynamic Damping and Young's Modulus in the Range of Rubberlike Elasticity. R. ECKER 859
Applied Force and Second Order Transitions of Rubber. F. T. WALL AND DONALD G. MILLER 876
Vulcanization Structures and Their Influence on the Heat Resistance and Fatigue of Rubber. B. A. DOGADKIN AND Z. N. TARASOVA 883
Dispersion of Fillers in Rubber. RUPRECHT ECKER 899
Polymerization Phenomena in the Vulcanization Process. B. DOGADKIN, M. FELDSTEIN, A. DOBROMYSLOVA, V. SHKURINA, AND M. KALPUNOV 920
Effect of the Molecular Weight of Rubber on the Kinetics of Vulcanization and on the Formation of a Spatial Network. A. S. NOVIKOV, G. M. BARTENEV, AND F. A. GALIL-OGLY 925
Dependence of the Fundamental Properties of Unvulcanized and Vulcanized Butadiene-Styrene Rubber Mixtures on the Initial Molecular Weight. A. S. NOVIKOV, M. B. KHAIKINA, T. V. DOROKHINA, AND M. I. ARKHANGELSKAYA 930
Electric Measurements of Rubber-Carbon Black Systems. GOTTHOLD KICKSTEIN 940
The Microstructure of Diene Polymers. I. Polyisoprenes and Polybutadienes Prepared at High Temperatures. W. S. RICHARDSON 954
The Microstructure of Diene Polymers. II. Polyisoprenes and Polybutadienes Prepared at High Pressures. W. S. RICHARDSON 958
The Microstructure of Diene Polymers. III. Polyisoprenes and Polybutadienes Prepared with Cationic Catalysts. W. S. RICHARDSON 961

Spontaneous Contraction of Rubber. II. Spontaneous Contraction of Rubber and Its Dependence on the Conditions of Testing, and Some Factors Concerned in Compounding and Technology. M. M. Reznikovskiĭ and M. K. Khromov 964
Mechanism of the Action of Accelerators of Vulcanization. Vulcanization of Rubber by a Sulfur Radioisotope. G. A. Blokh 974
The Effect of Masterbatching, Compounding, and Testing Variables on Constant-Slip Abrasion Results. L. H. Howland, W. W. White, and W. E. Messer .. 977
Air Permeability of Elastomers by Diffusion Tests. M. Czuha 996
The Plasticization of Rubber on Roll Mills. Eugene Stalinsky 1005
Choice of Solvent for the Viscometric Determination of Molecular Weights of High Polymers. L. H. Cragg, R. H. Sones, and T. E. Dumitru 1007
Chromatographic Analysis of Vulcanized Rubbers. Specific Methods for the Detection of Some Dithiocarbamate Accelerators. C. A. Parker and Joyce M. Berriman 1013
An Instrument for Determining the Relaxation and Recovery of Elastomers. B. G. Labbe and W. E. Phillips 1019
Measuring Wet-Gel Strength of Coagulant-Dipped Films. Paper Dip Method. A. I. Medalia, H. B. Townsend and H. N. Grover 1026
Possibilities in the Use of Sodium Chlorite in Latex. Josette Tournier 1041
Electron Microscopy of Hevea Latex Gels. A. J. de Vries and C. Ch. Dalitz 1047
Determination of Particle-Size Distribution in GR-S Latexes. Alfred Nisonoff, W. E. Messer, and L. H. Howland 1051
Rubber Hydrocarbon in Freshly Tapped Latex. G. F. Bloomfield 1061

RUBBER CHEMISTRY AND TECHNOLOGY

Rubber Chemistry and Technology is published quarterly under the supervision of the Editor, representing the Division of Rubber Chemistry of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

Rubber Chemistry and Technology may be obtained in one of three ways:

(1) Any member of the American Chemical Society may become a member of the Division of Rubber Chemistry by payment of the dues ($4.00 per year) to the Division and thus receive Rubber Chemistry and Technology.

(2) Anyone who is not a member of the American Chemical Society may become an Associate of the Division of Rubber Chemistry upon payment of $6.50 per year to the Treasurer of the Division of Rubber Chemistry, and thus receive Rubber Chemistry and Technology.

(3) Companies and libraries may subscribe to Rubber Chemistry and Technology at the subscription price of $7.50 per year.

To these charges of $4.00 and $7.50, respectively, per year, postage of $.20 per year must be added for subscribers in Canada, and $.50 per year for those in all other countries not United States possessions.

All applications to become Members or Associates of the Division of Rubber Chemistry, with the privilege of receiving this publication, all correspondence about subscriptions, back numbers, changes of address, missing numbers, and all other information or questions should be directed to the Treasurer of the Division of Rubber Chemistry, A. W. Oakleaf, Phillips Chemical Co., 318 Water St., Akron 8, Ohio.

Articles, including translations and their illustrations, may be reprinted if due credit is given Rubber Chemistry and Technology.

THE DIVISION OF RUBBER CHEMISTRY OF THE AMERICAN CHEMICAL SOCIETY

OFFICERS AND EXECUTIVE COMMITTEE

Chairman.....J. M. Ball, R. F. D. No. 1, Millstone Road, Wilton, Conn.
Vice-Chairman..A. E. Juve, B. F. Goodrich Research Center, Brecksville, O.
Secretary...A. M. Neal, E. I. du Pont de Nemours & Co., Wilmington, Del.
Treasurer.....A. W. Oakleaf, Phillips Chemical Co., Akron, O.
Editor of *Rubber Chemistry and Technology*....C. C. Davis, Boston Woven Hose and Rubber Co., Cambridge, Mass.
Advertising Manager of *Rubber Chemistry and Technology*....E. H. Krismann, E. I. du Pont de Nemours & Co., Akron, O.
Directors....J. C. Walton (Past Chairman), J. W. Snyder (Director-at-Large), L. M. Baker (Akron), W. S. Edsall (Boston), H. E. Elden (Buffalo), B. W. Hubbard (Chicago), G. R. Sprague (Connecticut), W. J. Simpson (Detroit), D. F. Reahard, Jr. (Fort Wayne), R. D. Abbott (Los Angeles), J. A. Breckley (New York), R. D. Ford (Northern California), T. W. Elkin (Philadelphia), F. W. Burger (Rhode Island), J. R. Wall (Southern Ohio), R. E. Harmon (Washington, D. C.).
Councillors....W. L. Semon, 1952–1955; A. M. Neal, 1955–1958 (Alternates, H. I. Cramer, 1952–1955; C. S. Yaron, 1955–1958).

COMMITTEES

Auditing....C. W. Christensen, *Chairman*; R. B. Appleby, R. H. Marston.
Advisory on Local Arrangements....C. M. Wolf, *Chairman*; S. L. Brams.
Bibliography....John McGavack, *Chairman*, V. L. Burger, D. E. Cable, C. C. Davis, H. E. Haxo, R. K. Kuhns, M. E. Lerner, A. W. Oakleaf, T. L. Wilson.
By-Laws Revision....C. S. Yoran, *Chairman*; A. M. Neal, W. L. Semon.
File and Records....J. D. D'Ianni, *Chairman*; Dorothy Hamlen, E. A. Willson.
Finance....L. V. Cooper, *Chairman*; S. B. Kuykendall, E. H. Krismann.
Education....R. G. Seaman, *Chairman*; W. B. Babcock, J. H. Fielding, H. L. Fisher, A. E. Juve, R. D. Stiehler, with additional members for local rubber groups sponsoring educational activities.
Future Meetings....A. E. Laurance, *Chairman*; G. M. Wolf.
Charles Goodyear Medal....J. C. Walton, *Chairman*.
Library....B. S. Garvey, Jr., *Chairman*; (Miss) Fern Bloom, (Miss) Lois Brock, (Miss) Dorris Hall, (Miss) Dorothy Hamlen, H. E. Simmons, H. N. Stevens, (Miss) Leora Straka, H. C. Tingey, R. F. Wolf.
Membership....T. A. Werkenthin, with a member from each local rubber group.
Nominating....S. G. Byam, *Chairman*; R. E. Bitter, S. M. Lillis, R. G. Seaman, M. Berman.

Papers Review....J. M. Ball, C. C. Davis, A. E. Juve, A. N. Neal.
Tellers....J. H. Fielding, J. Breckley, W. S. Edsall.

SPRING MEETING OF THE DIVISION OF RUBBER CHEMISTRY, LOUISVILLE, KENTUCKY, APRIL 14–16, 1954

The 65th Meeting of the Division of Rubber Chemistry was held in Louisville, April 14–16, 1954, with headquarters at the Brown Hotel. The meeting was attended by 878 members and guests.

The 25-Year Club met under the Chairmanship of Allyn Brandt, with approximately 150 present. The contest for the longest service in the rubber industry was won by Prosper Cholet (Allied Chemical).

At the Banquet, 655 members and guests were present. The highlights were a presentation of a Kentucky Colonelcy to the Chairman, J. C. Walton, by A. W. Grafton, representing the Governor of the State of Kentucky, and an address by C. E. Mannion, former Dean of Notre Dame Law School, on the preservation of freedom and human rights under the American system of government.

At the Executive Committee meeting, the following future meetings were approved.

Meeting number	*Dates*	*Place*	*Headquarters Hotel*
66	Sept. 15–17, 1954	New York	Commodore
67	May 4–6, 1955	Detroit	Sheraton-Cadillac
68	November 2–4, 1955	Philadelphia	Bellevue-Stratford
69	May 16–18, 1956	Cleveland	Cleveland-Carter
70	September 19–21, 1956	Atlantic City	*
71**	May 15–17, 1957	Montreal, Quebec	Sheraton-Mt. Royal

At the Business Meeting, recognition was made of the deaths, since the last meeting, of Charles Berlow, R. A. Crawford, H. L. Ericson, Etzio J. Giolito, George E. Griffin, M. B. Hart, George W. Miller, Oscar Nelson, Charles T. Schaffnit, Jr., D. A. Shirk, Hugh M. Smallwood, Thomas J. Starkie, and Joseph P. Zak.

The following papers were presented:

H-Substituted Alkylsulfenyl Dithiocarbamates as Accelerators of Rubber Vulcanization. J. V. Svetlik, H. E. Railsback, and C. C. Biard (Phillips Petroleum Co., Bartlesville, Okla.).

Accelerated Weathering of Various Elastomers, Using a Heliostat. G. H. Cosner and Ray Thoman (Gates Rubber Co., Denver, Colo.).

Effect of Sulfur and Accelerator Variation upon the Rate of Oxidation and the Deterioration of Properties of Rubber Vulcanizates. William L. Cox and J. Reid Shelton (Case Institute of Technology, Cleveland, Ohio.).

The Evaluation of Commercial GR-S Polymers by Means of the Creep Test. J. G. Lichty, R. B. Spacht, and W. S. Hollingshead (Goodyear Tire & Rubber Co., Akron, Ohio).

* Joint meeting with the parent society, no hotel arrangements yet.
** Joint meeting with the Rubber Division of CIC.

Laboratory Methods of Dynamic Testing of Compounds Containing Reclaimed Rubber. J. M. Ball and R. L. Randall (Midwest Rubber Reclaiming Co., East St. Louis, Ill.).

Changes in Branching and Distribution Effected by Milling Hot GR-S. W. K. Taft and June Duke (Government Laboratories, University of Akron, Akron, Ohio).

Particle Size in High-Solids Synthetic Latex. Maurice Morton and W. E. Gibbs (Rubber Research Laboratories, University of Akron, Akron, Ohio).

Oil Types in the Oil-Extended Rubber Program. W. K. Taft, M. Feldon, J. Duke, R. W. Laundrie, and D. Prem (Government Laboratories, University of Akron, Akron, Ohio).

Factors Influencing the Utility of Neoprene Cements. L. S. Bake (E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.).

Vulcanization of the W Type of Neoprene with Combinations of a Thiuram, a Guanidine and Sulfur. R. M. Murray and D. C. Thompson (E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.).

The Effect of Masterbatching, Compounding and Testing Variables on Constant-Slip Abrasion Results. L. H. Howland, W. W. White, and W. E. Messer (Naugatuck Chemical Division, U. S. Rubber Co., Naugatuck, Conn.).

The Influence of Surface Roughness and Porosity on the Performance of Carbon Blacks. E. M. Dannenberg and B. B. S. T. Boonstra (Godfrey L. Cabot, Inc., Boston, Mass.).

Continuous Hot-Air Vulcanization and Room-Temperature Vulcanization of Silicone Rubber. D. C. Youngs and G. M. Konkle (Dow Corning Corp., Midland, Mich).

Compounding of Silicone Rubber. III. F. L. Kilbourne, Jr., Clinton M. Doede, and Keistutis J. Stasiunas (Connecticut Hard Rubber Co., New Haven, Conn.).

Aging Stability of Neoprene Latex. II. The Relation Between Cross-Linking and the Hydrolysis of Allylic Chlorine. D. E. Andersen and P. Kovacic (E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.).

Improved Cross-linked Synthetic Rubbers. R. D. Gilbert, A. H. Krause, and N. R. Legge (Kentucky Synthetic Rubber Corp., Louisville, Ky.).

Control of Molecular Weight of Butadiene-Styrene Copolymers. I. C_4–C_{16} Mercaptans as Regulators. T. W. Boyer and N. R. Legge (Kentucky Synthetic Rubber Corp., Louisville, Ky.).

High Molecular-Weight Butadiene-Styrene Copolymers for Oil Extension. T. W. Boyer, R. D. Gilbert, and N. R. Legge (Kentucky Synthetic Rubber Corp., Louisville, Ky.).

NEW BOOKS AND OTHER PUBLICATIONS

Synthetic Rubber. G. S. Whitby, Editor-in-Chief; C. C. Davis and R. F. Dunbrook, Editorial Board. Published by John Wiley & Sons, Inc., 440 Fourth Ave., New York 16, N. Y. 1954. $6 \times 9\frac{1}{4}$ inches. xii + 1044 pages. Price, $18.00.—To call this book a milestone in the progress of the science of rubber is not to use a mere cliché, but only to describe the book justly. It is the first comprehensive and authoritative account of the subject, and marks the coming of age of synthetic rubber as a field of research and development. The Division of Rubber Chemistry of the American Chemical Society,

which initiated and sponsored its publication, can take merited pride in it. And the numerous authors are to be congratulated for the high quality of their contributions, and can rest assured that the book will be a boon to all scientific investigators. The editing too deserves praise. The different subjects have been kept in good proportion, despite the multiplicity of authors, and the book is acceptably up-to-date (it covers substantially all significant developments through 1935), in spite of the fact that the preparation of such a large collaborative volume inevitably requires a considerable period of time.

The Editor, G. S. Whitby, contributes an excellent introductory chapter, calculated to whet the appetite of the reader. In it he focusses attention on some high points and important unsolved problems to set the stage for the succeeding chapters. From this the reader proceeds, through the historical development of synthetic rubber, to methods of manufacture of raw materials for GR-S and Butyl rubber, including methods of manufacture of butadiene and isoprene not previously described. The manufacture of GR-S is described by J. W. Livingston and J. T. Cox, who were intimately associated with the wartime construction and operation of the GR-S plants. A full story of American work on emulsion-polymerization systems is contributed by C. F. Fryling.

The compounding and processing of GR-S is described by R. P. Dinsmore and R. D. Juve. Naturally, such an account cannot include all the vast number of individual softeners, accelerators, and pigments that a practical compounder may need, but the essentials of the subject are ably treated. The use of GR-S and other synthetic rubbers in certain special types of compounds, namely in wire and cable insulation and sheathing and in hard rubber, is discussed in separate chapters. A chapter by R. A. Crawford on the uses of GR-S surveys the different types of rubber products in which GR-S is just as satisfactory as, or more satisfactory than, natural rubber. This chapter, together with statistical data in the introductory chapter, show why rubber manufacturers in the United States are able to use synthetic rubber for a major portion of its requirements whenever the price of natural rubber rises considerably above that of GR-S.

The advent of synthetic rubber has, in recent years, inspired much new work on the physical testing of vulcanized rubber, and A. E. Juve presents a very useful discussion of this subject. Chemical methods for the study of the structure of diene polymers and copolymers are described by C. S. Marvel, who has done much to extend and refine the ozonolysis method. A description of physico-chemical methods for such studies is part of a notable chapter by L. A. Wood on the physical chemistry of synthetic rubbers.

A contribution by W. K. Taft and G. J. Riger on special diene polymers and copolymers shows how much territory has been covered in investigations to find whether any monomer other than styrene will give a copolymer with butadiene superior to GR-S. It deals also with synthetic rubber made, not by the emulsion process, but by catalysis with sodium, alfin catalysts, etc. Special types of synthetic rubber, including Neoprene, nitrile rubber, and Butyl, are treated fully in chapters by authors who have been intimately connected with their development. Newer types, e.g., the silicone and diisocyanate elastomers, are included.

There is an account of the important features of German manufacturing techniques and German research on synthetic rubber, and it is a just tribute to the pioneering German work in this field. But, at the same time, American chemists may justly feel great satisfaction from the fact that, in only thirteen

years, they have progressed so far in the development of synthetic rubber that their accomplishments form the major portion of the book.

The individual chapters are as follows. 1. Introduction, G. Stafford Whitby. 2. Historical Review, R. F. Dunbrook. 3. Manufacture of Dienes from Petroleum, C. E. Morrell. 4. Manufacture of Butadiene from Alcohol, W. J. Toussaint and J. L. Marsh. 5. Preparation and Production of Dienes by Other Methods, H. L. Fisher. 6. Manufacture of Styrene Monomer, J. E. Mitchell and J. L. Ames. 7. The Manufacture of GR–S, J. W. Livingston and J. T. Cox, Jr. 8. Emulsion Polymerization Systems, C. F. Fryling. 9. Chemical Study of the Structure of Diene Polymers and Copolymers, C. S. Marvel and H. E. Baumgarten. 10. Physical Chemistry of Synthetic Rubbers, L. A. Wood. 11. The Processing and Compounding of GR–S, R. P. Dinsmore and R. D. Juve. 12. Physical Test Methods and Polymer Evaluation, A. E. Juve. 13. Aging and Stabilization of GR–S, J. O. Cole. 14. Use of GR–S in Rubber Manufacture, R. A. Crawford. 15. Synthetic Rubber in Wires and Cables, J. T. Blake. 16. Synthetic Hard Rubber, F. S. Malm and Henry Peters. 17. Reclaimed Synthetic Rubber, F. L. Kilbourne, Jr. 18. Synthetic–Rubber Resins, J. D. D'Ianni. 19. GR–S Latex, L. H. Howland. 20. Latex Masterbatching, J. W. Adams and L. H. Howland. 21. Diene Polymers and Copolymers Other Than GR–S and the Specialty Rubbers, W. K. Taft and G. J. Tiger. 22. Neoprene, A. M. Neal and L. R. Mayo. 23. Nitrile Rubber, W. L. Semon. 24. Butyl Rubber, R. M. Thomas and W. J. Sparks. 25. Miscellaneous Synthetic Elastomers, C. H. Fisher, G. S. Whitby, and E. M. Beavers. 26. German Synthetic–Rubber Developments, R. L. Bebb and L. B. Wakefield.

"Synthetic Rubber" is indispensable to every serious student of rubber. Every rubber chemist and physicist should have a copy of his own and not be content to rely upon his library. He may not sit down with such a weighty book and read it through at once, but he will surely wish to read individual sections from time to time. Whether engaged in research or in development work, he will find repeated occasions to make use of the vast store of information in the book, which is enhanced by its comprehensive index and bibliographies.

Finally, in recognition of the publisher, the general character of the book and its attractive blue buckram binding deserve commendation.

Bibliography of Rubber Literature for 1946–1948. Division of Rubber Chemistry, American Chemical Society. Division treasurer—A. W. Oakleaf, Phillips Chemical Co., 318 Water St., Akron 8, O. Cloth, 6 by 9 inches, 484 pages. Price to nonmembers, $5.—This eighth edition of the "Bibliography" brings the total coverage of the series to the period 1935–1948. The series is expected to be up to date by 1957, but even at this incomplete stage it continues to be of incalculable value to all technical men in the rubber field. The current edition contains more than 5,950 references to patents and literature, compared with 4,903 in the 1944–1945 volume. The general format remains the same: references are classified into groups, and brief abstracts appear for each; and comprehensive author and subject indexes are included.

Fachkunde für die Gummi industrie. Vol. I. Werkstoffkunde. (Technology of the Rubber Industry. Vol. I. Materials.) Edited by Arthur Springer. Published by Fachbuchverlag GmbH, P. O. Box 67,

Leipzig W. 31, East Germany. 6½ by 9 in. 342 pp. DM 12.00 (approximately $3.00). (In Germany).—The first of ten planned volumes intended to serves as a "guide" to the rubber industry, this book is devoted to materials. It is basically a textbook designed for the educational training of qualified rubber workers.

The technical portion of the book, which is fortunately the greater part, starts with raw materials and extends through softeners, fillers, etc., to sponge rubber, textiles in the rubber industry, and latex technology. The book attempts to acquaint the student, in popular fashion, with any and all materials used in the filed. There are chapters about Buna as well as "Synthetic Rubbers of Foreign Countries," about thioplasts as well as silicones, about vulcanization, reclaiming, testing methods, solvents, etc. This portion of the book indicates an extraordinary theoretical and practical knowledge of the topics mentioned. Whether the data are too specialized to be mentally digested by young workers without adequate scientific training is the concern of the compilers. From this reviewer's viewpoint, the technical part of the book seems to be a worthwhile contribution to the literature.

Abstracts of Technical Papers from the Government Synthetic Rubber Program. Office of Synthetic Rubber, Federal Facilities Corp., Washington 25, D. C. $5 per set, paper covers.—A four-volume compilation of abstracts covering papers published during 1942–1952 has been prepared by M. H. Forsythe and S. C. Wacker, of the Technical Publications Branch, Research & Development Division, Office of Synthetic Rubber, under the supervision of Paul S. Greer, chief of that Division. The assistance of Harry L. Fisher and Walter W. Rinne in reviewing the abstracts is acknowledged.

The volumes include a summary of synthetic rubber research performed by university, industrial, institute, and government groups participating in the synthetic rubber research program. Author and subject indexes are included. Abstracts for the paper published during 1953 are currently being prepared, and issuance will be made in the near future.

What Every Engineer Should Know About Rubber. By W. J. S. Naunton. Published by the British Rubber Development Board, Market Buildings, Mark Lane, London E. C. 3, England. Available from Natural Rubber Bureau, 1631 K Street, N.W., Washington 6, D. C. 5½ by 8½ in. 128 pp. 50c.—The purpose of this book is to provide necessary information to enable the engineer to make effective use of rubber. Despite the fact that it numbers only 128 pages, the book presents a broad cross-section of information on rubber, written entirely with the engineer's working day in mind. The author, formerly in charge of the rubber laboratories of Imperial Chemical Industries, Ltd., and an internationally recognized rubber technologist, has had many contacts with engineers through the years, with the result that he is able to approach the subject from the point of view of the engineer who wants to incorporate rubber in his designs. Over half the book is devoted to specific engineering uses of rubber, while the sources, properties, manufacture and testing of rubber are covered in the remainder. The chapter on manufacture has been included to enable the engineer to acquire the necessary background knowledge of the material. Although intended solely for the engineer, and containing a good deal of basic information, this little volume will prove a valuable addition to the technical literature.

RAW MATERIALS FOR ELECTRIC CABLES. By A. King and V. H. Wentworth. Published by Ernest Benn, Ltd., Bouverie House, Fleet St., London, E.C. 4, England. 5½ by 8½ in. 362 pp. Price: 42s (approximately $6.00).—Published as a result of the widespread interest which stemmed from a series of articles written by the authors some time ago in *The Electrical Journal*, this book deals with raw materials used in electric cable manufacture, their sources and characteristics, and the tests to which they are subjected before acceptance. Since the authors' prime experience lies in the field of power and rubber and pastics cables, respectively, several of the chapters are co-authored with other experts with more direct experience in specific branches of the field, such as aluminum, copper, lead, textile insulants, asbestos, enamelled wire and quality control.

The book has 24 chapters: (1) Copper; (2) Paper; (3) Insulating Oils and Compounds; (4) Black Varnished Cambric; (5) Natural Rubber; (6) Rubber Compounding Ingredients; (7) Gutta-Percha; (8) Synthetic Rubbers; (9) Polyethylene; (10) Polytetrafluoroethylene; (11) Polyvinyl Chloride; (12) Lead; (13) Aluminum; (14) Armor and Reinforcement; (15) Steel; (16) Textiles; (17) Textile Insulants; (18) Wax Impregnants for Textile Insulants; (19) Lacquers; (20) Impregnants for Cable Finishes; (21) Inorganic Materials; (22) Enamelled Wire; (23) Compensating Leads for Thermocouples; (24) Quality Control. It should be evident from these titles that the book is a comprehensive treatise on the raw materials used in electric cables and is a valuable edition to the technical literature on insulated wire and cables in general.

LE CAOUTCHOUC DANS LA ROUTE. (RUBBER IN ROADS). Issued by Edition R.C.P., 37 Rue Taitbout, Paris 9, France. 7 by 9½ in. 28 pp. (In French).—As indicated by its title, this booklet is devoted to the application of rubber in roads. Actually, it consists of six short chapters outlining specific experiences with rubber on roads in various European countries, including France, Great Britain, Holland, and Italy. Each chapter has been furnished by an expert familiar with installations in his own country. Experiences include not only installations but special tests to determine performance. Data on results ascertained to date are also included. Numerous photographs are utilized to strengthen the text.

HEVEA DISEASES OF THE AMAZON VALLEY. By Mitchel H. Langford. Issued by Instituto Agronomico do Norte, Belem, Brazil. 6¼ by 9 in. 28 pp.—Since its establishment in 1940, the Instituto Agronomico do Norte has conducted investigations on Hevea rubber. One phase of this program has been to study the major Hevea diseases and to develop satisfactory control measures against them. Brief descriptions of these diseases and the measures that have been found effective against them are given in this booklet. Among the diseases discussed are South American Leaf Blight, Phytophthora Pod Rot, Target Leaf Spot, Glomerella Die-Back, Black Crust, Pink Disease, and various root diseases. Excellent photographs depicting these diseases and their effect are reproduced. The author, Michael G. Langford, is the principal pathologist of the Division of Rubber Plant Investigations of the U. S. Department of Agriculture and a long-time collaborator of the Institute. A reprint of the article on "Hevea Diseases of the Western Hemisphere," which appeared in a recent issue of the *Plant Disease Reporter*, is also available from the Institute on request.

ASTM STANDARDS ON PLASTICS. May, 1954, American Society for Testing Materials, 1916 Race St., Philadelphia 3, Pa. Heavy paper cover, 6 by 9 inches, 741 pages. Price, $5.75.—One hundred and forty-two ASTM standards are in this latest compilation, including 92 test methods, 32 specifications, 14 recommended practices, and 4 lists of definitions relating to plastics, methods of mechanical testing, and conditioning and weathering. Standards cover properties; analytical methods; molds and molding processes; conditioning; plates, sheets, tubes, rods, and molded materials; and electrical tests.

The new material section includes specifications and test methods for: cellulose acetate sheet and film for primary insulation; nonrigid thermoplastic compounds for automotive and aeronautical applications; shrinkage of molded and laminated thermosetting plastics at elevated temperature; tension testing of vulcanized rubber; and measuring water-vapor transmission of materials in sheet form.

THE SULFUR DATA BOOK. Edited by William N. Tuller, of Freeport Sulphur Co. McGraw-Hill Book Co., 330 W. 42nd St., New York 36, N. Y. Cloth, 6 by 9 inches, 140 pages. Price, $5.00.—A compilation of technical data on sulfur, this book presents material from literature, from private sources, and from the experience gained by Freeport during its 40 years' production. This marks the first time that a comprehensive collection of such information is available under one cover.

The text is broken down into five major sections—the nature of sulfur, its physical and chemical properties, reaction thermodynamics, solubilities, and methods of analysis. Numerous diagrams, tables, and graphs are used to illustrate the text.

A FRENCH–ENGLISH DICTIONARY FOR CHEMISTS. By Austin M. Patterson. Second Edition. Published by John Wiley & Sons, Inc., 440 Fourth Ave., New York, 1954. Cloth, 5¼ by 7¼ inches. 476 pages. Price, $6.50.—Twenty years is a long time to wait for a new edition of the most reliable, the most useful, and, in spite of its small size, the most comprehensive French-English dictionary for chemists ever published. But now the patience of these chemists is well rewarded by a still more comprehensive dictionary which will make it even easier for those with only a limited command of the language to read scientific and technical French easily and accurately.

The number of entries has increased from 35,000 to 42,000, including important nontechnical and nonscientific expressions encountered in the scientific and technical literature. An unusual feature is a discussion of the peculiarities of French chemical nomenclature, and of great help and especially worthy of commendation is the inclusion of irregular forms of words, particularly verbs, with their actual spelling rather than their parent forms. Many terms no longer in use are included to aid in reading the older literature.

As further evidence of the authoritativeness of the dictionary, the most recent decisions of the International Union of Applied Chemistry have been followed in the choice of English terms.

This dictionary is a worthy companion volume to Patterson's highly esteemed German-English dictionary, and should be a welcome addition to the reference library of every chemist.

PHOTOELASTIC STUDIES CONCERNED WITH FATIGUE PHENOMENA IN RUBBER ARTICLES *

ATTILIO ANGIOLETTI

SOCIETÀ PIRELLI P.A., MILAN, ITALY

INTRODUCTION

The resistance of certain rubber articles to repeated stresses depends both on the properties of the mixtures themselves and on the local deformations; in fact, it is sufficient that even a small section be subjected to an undue concentration of forces to endanger the life of the article.

Hence it is advisable to know the relative distribution of deformations in order to alter this distribution by changes of the shape of the article for the purpose of improving its fatigue resistance.

Objects made of highly deformable materials, in particular those of rubber, are generally designed on a purely empirical basis; a rigorous treatment of such a problem is difficult, since some of the most important hypotheses of the theory of elasticity, on which the science of construction is based, are not valid in this field.

Two possibilities then present themselves:

(1) Calculations based on a theory of elasticity of high deformations. The numerous attempts of various investigators in this direction provide a solution only of simple problems, while the mathematical difficulties are still considerable.

(2) The prosecution of an actual experiment.

It appears to us that, among possible methods, a photoelastic test can be considered a suitable method.

This method is based on the optical anisotropy which appears in some transparent materials when they are subjected to stress (photoelasticity). Some transparent mixtures have this property, and many authors[1] have studied them, particularly from a theoretical viewpoint.

The applications of photoelasticity to the study of slightly deformable structures, that is, those in which the deformations can be considered infinitesimal with respect to the dimensions of the structure studied, are numerous, and the literature on this subject is extensive[2].

On the other hand, applications of photoelasticity to the study of highly deformable solids have been rare. In this connection, however, attention should be called to a study of some samples adapted to rubber technology by Hurry and Chalmers[3].

THE PHOTOELASTIC METHOD

Before passing to a brief description of the photoelastic method, a few definitions of the terms used should be given.

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the original version in Italian of the paper in German in *Kautschuk und Gummi*, Vol. 6, No. 9, pages WT 171–177 (1953).

The principal directions are the three spatial directions, perpendicular to each other, according to which at any point and for any type of force only a normal stress acts; in the plane there are two principal directions and the normal stress corresponding to each is a maximum or minimum with respect to those which act in the other directions.

The *principal stresses* are the normal stresses which act along the principal directions.

The *principal deformations* are the deformations corresponding to the principal stresses in an isotropic substance.

The *isostatics* are lines the tangents of which at every point on them are the principal directions at the points themselves.

The photoelastic method makes it possible to study the principal directions and stresses at all points of a body subjected to stress. In the most complicated cases, three-dimensional photoelasticity, which involves notable difficulties, must be used; on the other hand, when it is possible to consider the problem in one plane, the method becomes relatively simple.

In this case, the only one considered in the present work, recourse was had to plane models of constant thickness, which represent a cross-section of the material studied, subjected to forces in the same plane.

A ray of polarized monochromatic light which passes through a sheet of transparent isotropic material perpendicular to its plane is resolved, when the sheet is subjected to stress, into two vibrating rays in perpendicular planes, whose traces on the sheet coincide with the principal directions.

The two rays emerging are also out of phase with each other by an angle:

$$\varphi = \frac{2\pi \cdot C \cdot e(p - q)}{\lambda} \tag{1}$$

where C is a photoelastic constant depending on the material, which is experimentally determined; e is the thickness of the sheet, $p - q$ is the difference between the principal stresses, and λ is the wave length of the light. The two rays are again in phase when

$$\varphi = 2K\pi, \quad \text{i.e.,} \quad p - q = \frac{K\lambda}{C \cdot e} \tag{2}$$

where K is a whole number which can have the values $1, 2 \ldots n$. At those points where Equation (2) is satisfied, the polarized light is reestablished in the plane of the incident ray, which is then extinguished by the analyzer.

The geometric location of the points where, for a given value of K, Equation (2) is valid, is a line or a zone which may be designated as an isochrome; in it the difference between the principal stresses is constant.

An isochrome corresponds to every value of K, and K defines its order. The lines of increasing order $1, 2 \ldots n$ correspond to differences between the principal stresses. It is then possible, by various methods, to deduce from these differences the effective value of the principal stresses.

Operating with white light, one obtains colored lines instead of dark lines; since white light consists of a continuous progression of radiation of differing wave lengths, the radiations of wave length will be extinguished at every point.

$$\lambda = \frac{C \cdot e}{K} \cdot (p - q) \tag{3}$$

The isochromes therefore appear in the complementary colors of the extinguished.

Isoclines.—In some cases one of the principal directions at a point on the sheet coincides with the plane of polarization of the incident ray. The latter is then not resolved and is extinguished by the analyzer; the location of the points where one of the principal directions is parallel to the polarization plane of the incident ray is defined as a line or isoclinic zone.

These lines vary in position according to the angle formed by the polarization plane of the incident ray with an angle taken as a reference angle. From the isoclines, it is possible to determine the course of the isostatics by simple geometric construction.

APPLICATIONS OF THE METHOD TO THE STUDY OF HIGH DEFORMATIONS, PARTICULARLY IN RUBBER MODELS

In order to study highly deformable solid substances (rubber), it is necessary to use highly deformable models.

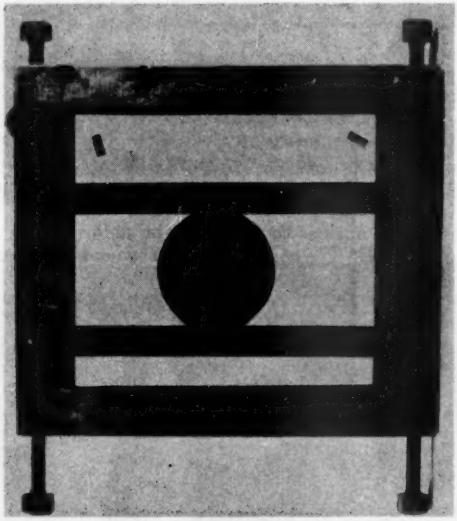


FIG. 1.—Metal frame for holding the models to be examined.

The study of a model which represents the cross-section of a solid subjected to stress represents a special case because of its great deformability.

If the model is subjected to tension, it remains flat, but decreases in thickness in a way which depends on the system of forces applied, and on its external form. In this case, only qualitative measurements are possible.

If the model is subjected to compression, there will be lateral flexures due to its thinness (necessary for good transparency) or in any case an increase of thickness.

To avoid either an increase of thickness or, above all, lateral flexure by compression, the test-specimens were placed between parallel glass plates, whose inner walls were at a distance equal to the thickness of the models, and held fast by a metal frame (Figure 1).

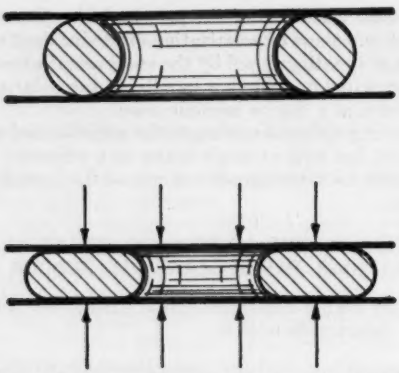


FIG. 2.—Undeformed cross-section and compressed cross-section of the cylindrical ring.

The inner walls of the glass plates must be well lubricated with castor oil or glycerine in order to eliminate tangential tensions on the stressed model.

The reader may picture, for example, a ringe with circular cross-section, compressed between two parallel plates (see Figure 2); if the mean diameter of the ring is great enough compared to the diameter of the cross-section, the latter can be regarded in an approximate way as part of a cylinder of infinite height.

Since the forces are normal to the axis, the deformations also remain in planes normal to the axis. The compression of the model between two plates of

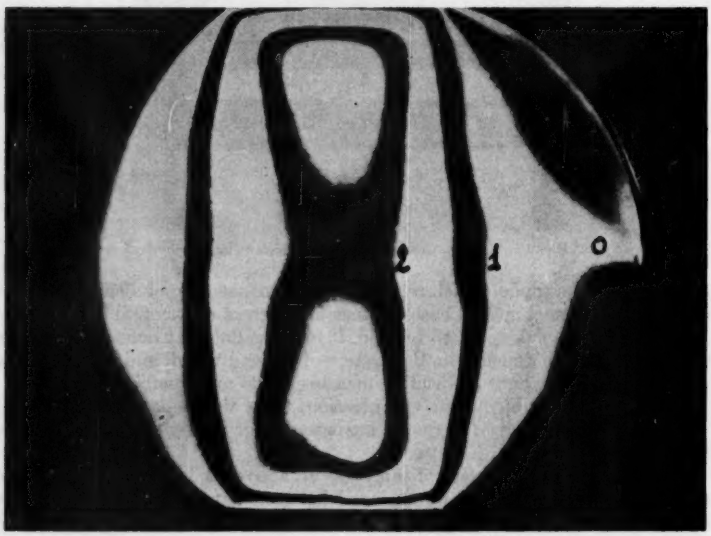


FIG. 3.—Isochromes of the cross-section of the toroidal ring under 10 per cent compression.

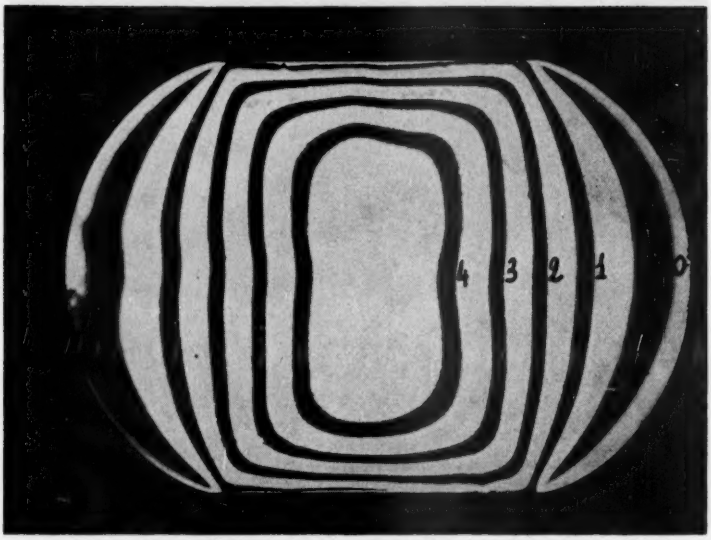


FIG. 4.—Isochromes of the cross-section of the toroidal ring under 20 per cent compression.

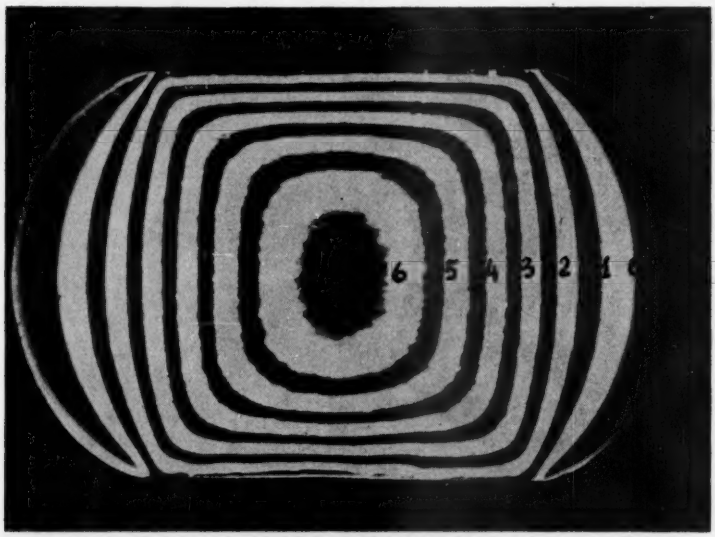


FIG. 5.—Isochromes of the cross-section of the toroidal ring under 30 per cent compression.

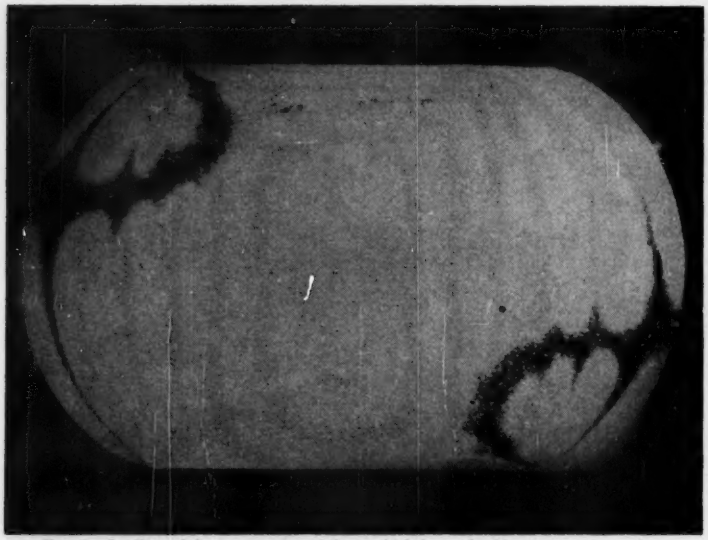


FIG. 6.—Isoclines of the cross-section of the toroidal ring under 30 per cent compression.

glass does not alter the deformations which would take place in the infinitely tall cylinder.

In order to study the distribution of deformations in this cross-section, it is necessary to construct a transparent rubber model, in this case a disk several millimeters thick.

After the disk is placed between the glass plates, it is compressed in a way similar to a cross-section of the ring. The isochromes and isoclines can be seen by a crossed nicol prism.

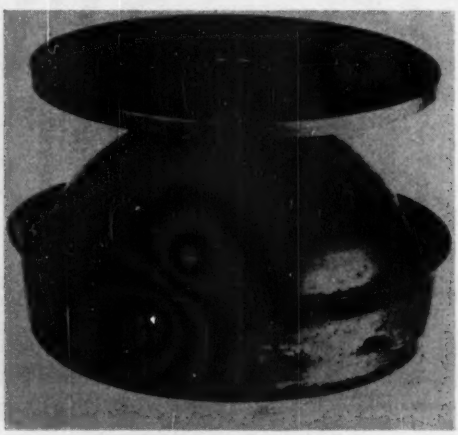


FIG. 7.—Shock absorber for trucks.

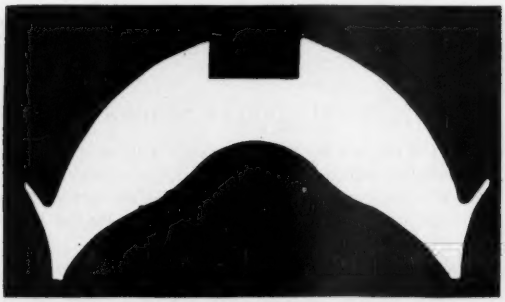


FIG. 8.—Metal form for the model shock absorber shown in Figure 7.

Figures 3, 4, and 5 show the isochromes and the relative orders for 10, 20, and 30 per cent compression; in Figure 6 the isoclines are shown only where the angle formed by the polarization plane of the light, referred to the vertical, is 15°.

This is an example of a simple model; models, however, may have any shape whatsoever, even with metal parts rigidly bonded to rubber parts; in all cases they represent cross-sections of solid specimens of infinite length.

If one wishes to study the axial cross-section of a rotating body by means of a model of this type, an inexact picture of the state of deformation of the cross-section itself will be had; the lack of precision depends on the degree of deformation of the specimen perpendicular to the plane of the cross-section examined.

Nevertheless, various observations have been made on models representing axial cross-sections of rotating solids, and in these cases the state of deformation

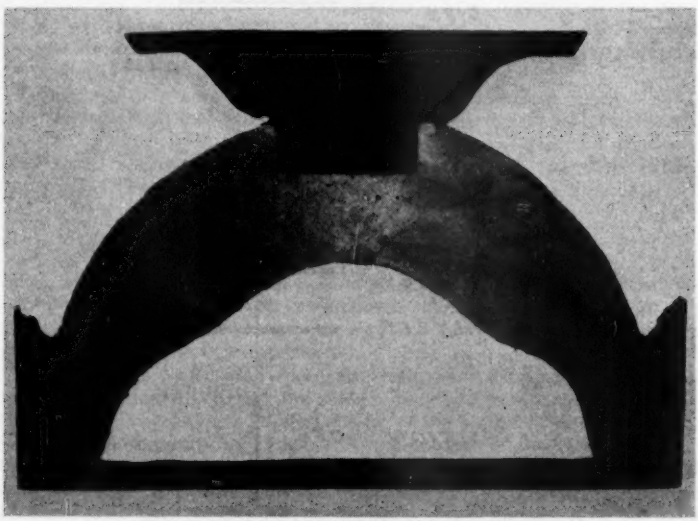


FIG. 9.—Cross-section of the model shock absorber.

of the model does not coincide with that of the cross-section of the solid. Nevertheless, photoelastic observation makes it possible to identify the most highly stressed zones.

CONSTRUCTION OF MODELS

The construction of models is quite simple; a section is cut out from a sheet of aluminum of thickness equal to that of which the model is to be made (from 2 to 5 mm.), with the same configuration as the cross-section to be studied.

Figure 7 represents a bell-shaped shock absorber, Figure 8 the axial cross-section of the model, and Figure 9 the model itself.

The transparent mixture used had the following composition:

Pale crepe rubber	100
Tetramethylthiuram disulfide	0.35
Diphenylguanidine	0.5
Stearic acid	0.5
Zinc oxide	1.0
Sulfur	2.0
Optimum cure 50 min. at 122° C	

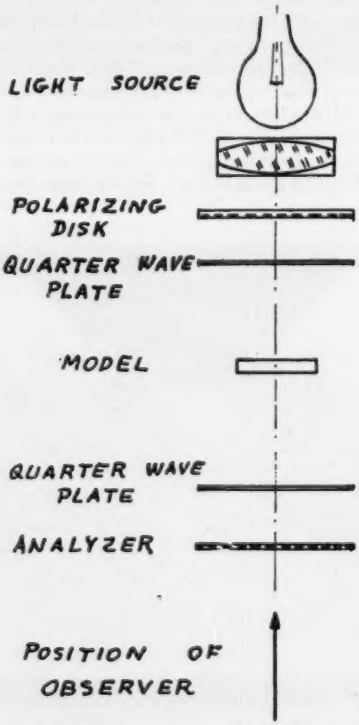


FIG. 10.—Schematic representation of the polarization apparatus.

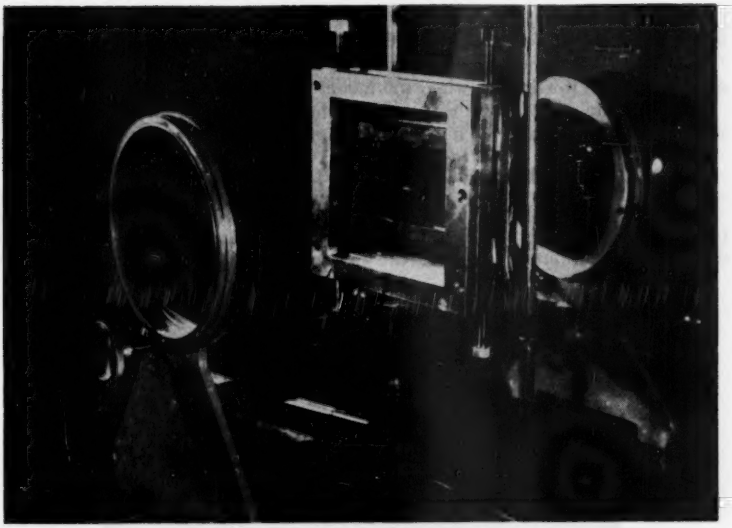


FIG. 11.—Apparatus for observations in polarized light.

APPARATUS FOR THE STUDY IN POLARIZED LIGHT

The apparatus for the photoelastic examination consists of a device holding two parallel and coaxial polaroid disks of about 15 cm. diameter, 50 cm. apart, mounted so that they can be rotated simultaneously about their axes by means of a single lever; they are oriented so that a ray of light falling on the first polarizer is extinguished by the second.

Illumination is obtained by means of a 100-watt sodium-vapor lamp for monochromatic light and a 1000-watt incandescent lamp for white light. Between the light source and the first polarizer there was placed a condenser, about 18 cm. in diameter, to obtain a bundle of sufficiently parallel light rays (Figure 10). The model is put between the two polarizers (Figure 11).

STANDARDIZATION OF THE MODELS

By gradually loading the model, it is possible to test the formation of successive isochromes and establish the order; in some cases the isochromes of increasing or decreasing order are so numerous and close that the use of a microscope in counting them is indispensable.

The isoclines are also easily seen, especially with models 2–3 mm. thick; they can be eliminated by inserting two properly oriented quarter-wave plates between the polarizers on the opposite sides of the model. The same result is obtained in photography by rotating the polarizers 90° during the exposure. Although the isoclines are connected to the angle formed by the plane of polarization with a given direction, the isochromes depend only on the difference in the optical path between the two rays emitted from the model; if the polarization plane rotates rapidly in the time interval (circular polarized light emitted

from the first quarter-wave plate), the isoclines are no longer visible, while the isochromes remain perfectly evident.

On the other hand, it is impossible to observe the individual isoclines by eliminating the isochromes when the model is greatly deformed.

At any rate the obstacle can be overcome by photographing in white light with suitable plates and by long exposures.

STANDARDIZATION OF THE MATERIAL USED FOR THE MODELS

In the general case of a model made of lightly deformable material, it is possible, given the order of an isochrome and by means of Equation (1), to determine the difference between the two principal stresses $(p - q)$ which act

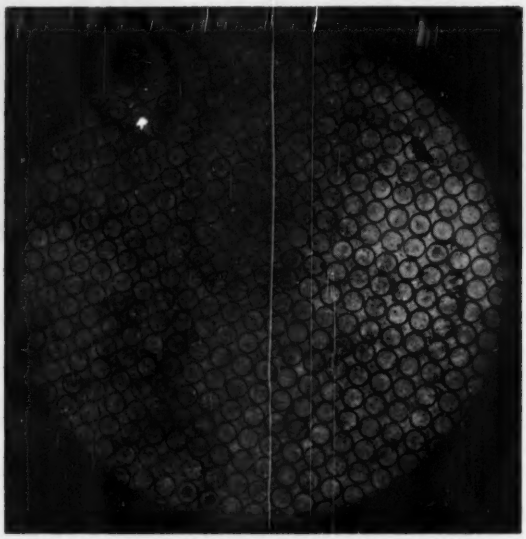


FIG. 12.—Example of a test-specimen for the determination of the photoelastic constants of a material.

in the plane of the model to which correspond deformations ξ_p, ξ_q coplanar with p and q, and ξ_r, perpendicular to the first two.

The stress r, perpendicular to both p and q, is zero, because the model is loaded, as was said before, only by forces acting in the same plane.

In the case of the highly deformable rubber model placed between glass plates and subjected to compression by forces acting in the same plane, a stress r acting against the plates themselves is also produced, to which an ξ_r deformation of zero corresponds.

The material must, accordingly, be standardized with specimens subjected to stress under the same conditions as the rubber models.

Various types of specimens, in the form of disks, straight prisms, etc., were made. On the surface of these, small rings, of about 3 mm. diameter and with thin sides, were impressed directly by vulcanization so as not to interfere in the distribution of the deformations in the loaded specimen (Figure 12).

Each disk placed between the glass plates was compressed between two parallel planes tangent to the lateral cylindrical side surface; each prism was compressed between opposite bases. In the center of these specimens deformation is quite uniform; hence, it is possible to determine for different compressions both the order of the isochrome and corresponding maximum (ξ_p) and minimum (ξ_q) deformations of the ring lying along it by means of a 10-power microscope having an ocular scale.

Plotting the orders of the isochromes and the corresponding values of ξ_p and ξ_q (obtained from the axes of the ellipse which develops from the ring), the characteristics of the material become evident.

The results, shown in Figure 13, lead to the following observations:

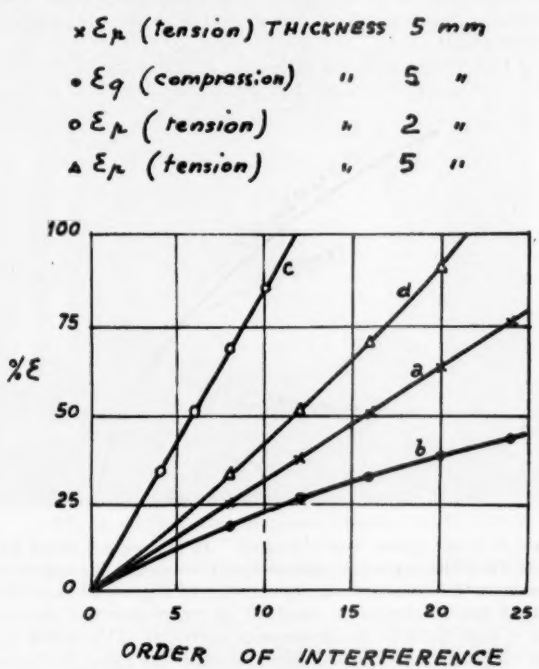


FIG. 13.—Standardization curves of a material.

(1) The order of an isochrome is practically a linear fraction of ξ_p, at least within deformations of the order of 100 per cent, for which Equation (1) becomes

$$\varphi = \frac{2\pi \cdot C_1 \cdot e \cdot \xi_p}{\lambda} \tag{4}$$

It can be established that this result is very close to that derived from the relation indicated by Treloar[4] where

$$n_1 - n_2 = C_2[(1 + \xi_p)^2 - (1 + \xi_q)^2]$$

$n_1 - n_2$ is the difference between the indexes of refraction of the material relative to the two directions of vibration of the polarized rays emitted from the model, e is the thickness of the model, and C_1 and C_2 are constants.

(2) What has been said above does not depend on the pressure exerted by the material on the inner walls of the glass. Not being able to measure this pressure, one must be satisfied with knowing only the state of deformation at every point of the cross-section tested.

The experimental precision is such that the ordinates of curve c for a model 2 mm. thick, multiplied by $\frac{2}{3}$ give curve a; the relation between the thicknesses of the models of curve c and curve a is $\frac{2}{3}$.

The order of an isochrome is then, with equal values of ξ_p, directly proportional to the thickness of the specimen, according to Equation (4).

Other standardized tests of models subjected to various stresses gave in all cases the same result.

Finally a test was carried out with a small prismatic bar-shaped specimen, 5 mm. thick, subjected to simple tensile stress. Curve d of Figure 13, the

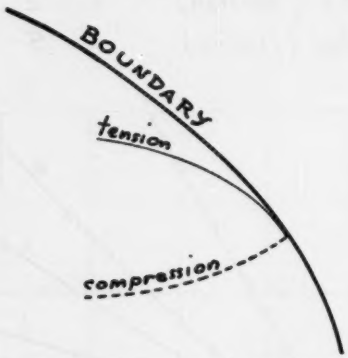


FIG. 14.—Tensile isostatic tangent to the profile of the model.

course of which is not linear, was obtained. In this case it must be taken into consideration that the material contracts as the tension increases.

In order that the standard curves a and c of Figure 13 may be valid, it is necessary that the thickness be constant at every point of the cross-section tested, that is, that there be no increases or decreases of thickness in the model. There must be no increases of thickness because the glass plates are carefully kept at a constant distance apart, equal to the thickness of the model. On the other hand, decreases can take place at the points where the principal compression is very small or zero, as occurs along the exterior of the model when the isostatic of tensile stress is tangent to it.

In this case, since the profile must be under no stress for a state of equilibrium, the principal compression will be zero, while the principal tension will cause a decrease of thickness of the model; here the material is subjected to simple tensile stress (Figure 14).

It is possible to proceed from the order of the isochrome at that point of the exterior profile to the value of the local deformation, referring to Figure 13, curve d. There is still some uncertainty concerning the inner points near the

profile and separated from the glass plates where the material is not subjected to simple tension; at these points, the deformations will be included between the ordinates of curve d and curve a.

FATIGUE TESTS

Now that the possibility of learning the principal directions and the deformations along them at every point on the plane of the cross-section of the material tested has been established, it is advisable to indicate in which zones the harmful effects of fatigue are most felt. The conclusions which were reached

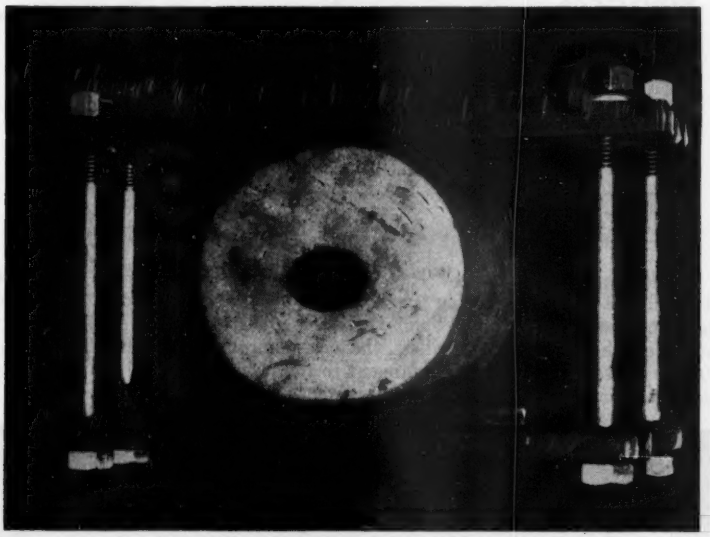


FIG. 15.—Hollow cylinder compressed between two parallel plates.

by means of various tests and by studying various conditions can be summarized as follows.

(1) Fatigue cracks are observed where an isostatic, along which the material is extended, is tangent to an external profile; they thus leave the surface and are propagated inward, depending on changes in the course of the isostatics themselves as rupture proceeds. The rapidity with which they begin depends on the degree of local deformation.

(2) The most heavily stressed points, if not on the surface, do not coincide with those most subject to fatigue effects.

(3) Cracks appear in the form of fissures perpendicular to those of tensile stress.

These statements are true of correctly made objects and do not take into consideration possible discontinuous rubber-metal surfaces where separation is possible.

A few of the cases studied will now be briefly described.

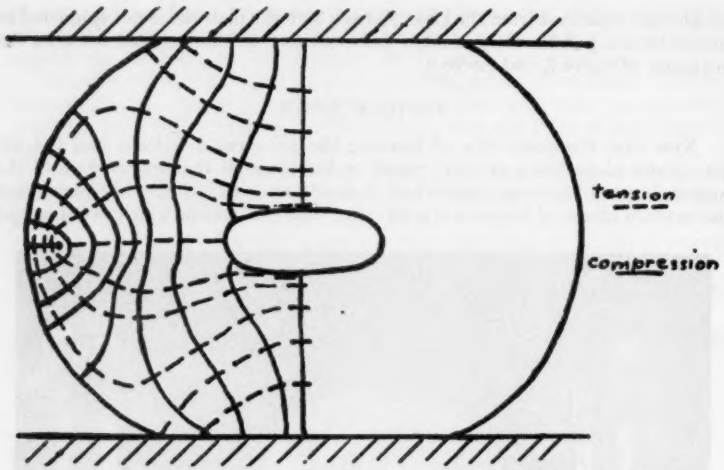


FIG. 16.—Isostatics of the hollow cylindrical model compressed between two parallel plates.

Hollow cylinder compressed between parallel planes (Figure 15).—The points at which the local deformation is greatest are located at the two extremities of the compressed inner central hole, where the curvature of the profile is greatest; where the curvature is smallest, the local deformation is somewhat smaller, but the isostatics of tension are tangent to the profile (Figure 16). There the rupture indicated in Figure 17 was obtained.

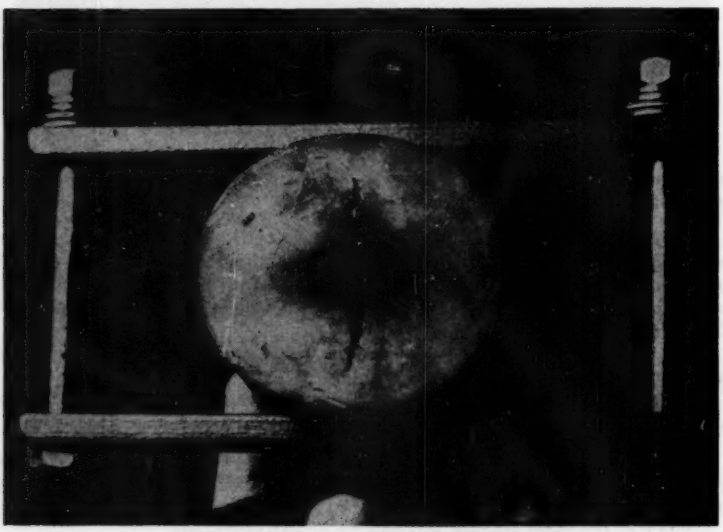


FIG. 17.—Cracks from fatigue of the hollow cylindrical model.

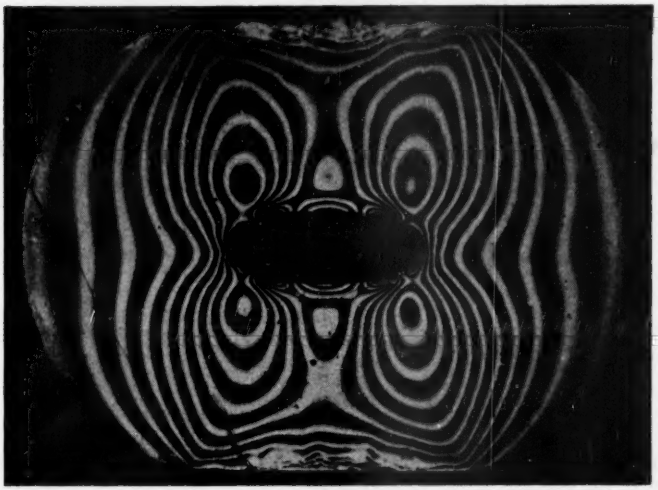


FIG. 18.—Isochromes of the hollow cylindrical model compressed between parallel planes.

The isochromes are shown in Figure 18 (model 5 mm. thick).

Truck shock absorbers.—The isochromes and isostatics observed on a model (2 mm. thick) of the axial cross-section of this shock-absorber, compressed 50 per cent, are shown in Figures 19 and 20. It can be established that in this case, too, the points which first showed fatigue ruptures are situated where the isostatic along which the material is extended, is tangent to the external profile (Figure 21).

One of these tires showed internal fractures after an undetermined operating time (Figure 22 in cross-section). Figure 23 represents the isochromes photographed on a model 2 mm. thick, and Figure 24 the isostatics. It can be seen that the profile of the internal channels, in which a metallic cable is contained, appears extended at two opposite points; the fractures, which are quickly propagated to the inside of the tire, probably begin here.

Let us again consider the shock absorber in Figure 7; several variable factors were tested in order to improve its fatigue resistance. It was found that

FIG. 19.—Isochromes of the model shock absorber for motor cars.

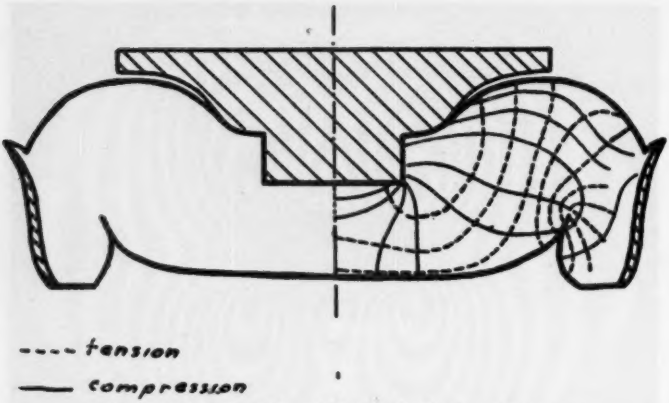


FIG. 20.—Isostatics of the model shock absorber for motor cars.

the design indicated in Figure 25 does not show tangents on the profile in the plane of the isostatic model (Figure 26).

Fatigue tests were made on these shock absorbers by compressing them dynamically from 0 to 40 per cent at a frequency of 8 cycles per second. The original shock absorber showed an average duration of 20 hours, while the modified one underwent stress for 900 hours without the appearance of any rupture.

Other experiments indicated that the results of these tests are modified, though not reversed, by the imposition of a moderate static load on the dynamic load.

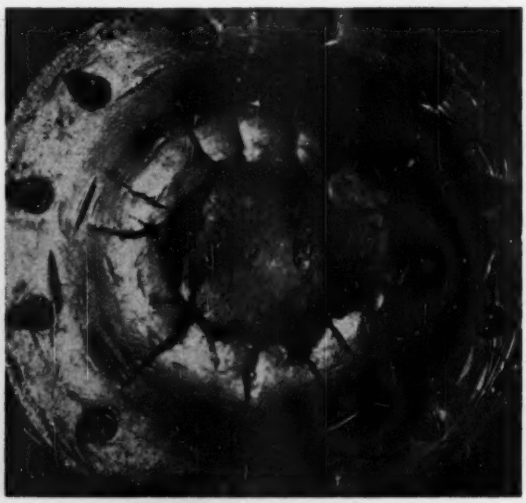


FIG. 21.—Cracks from fatigue of the model shock absorber for motor cars.

FIG. 22.—Cracks from fatigue in a solid tire.

Finally, the case of the ring of cylindrical cross-section in Figure 2, compressed 30 per cent, should be noted. In the cross-section considered, there are no tension isostatics tangent to the external profile, for which a resistance to the exceptional fatigue is predictable under these conditions (Figure 27). However, after a certain compression, there will be tension isostatics tangent to the external profile, but the superficial deformations will still be very low, and the danger of fatigue rupture will be very slight.

The ring of circular cross-section when compressed then represents an excellent application of the material, both because the parts most heavily stressed

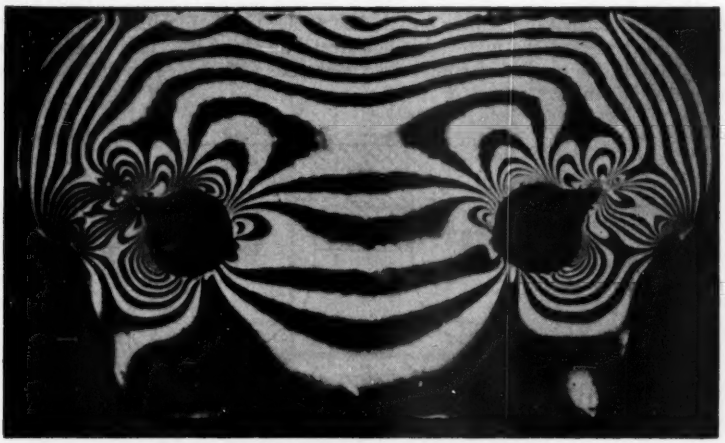


FIG. 23.—Isochromes of the cross-section of a solid tire.

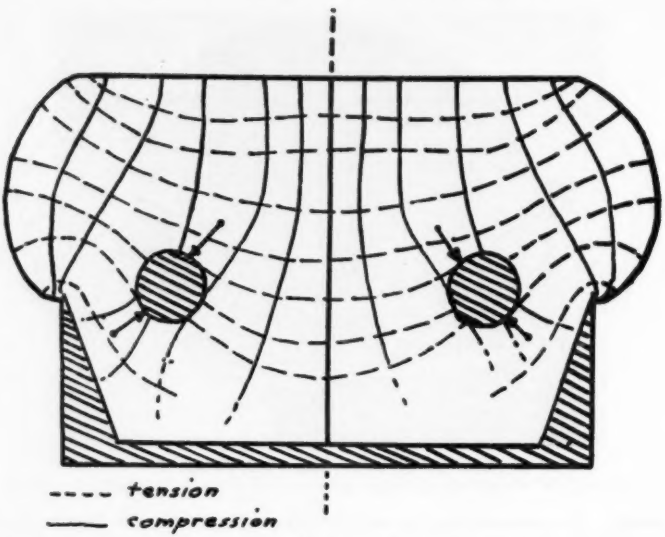


FIG. 24.—Isostatics of the cross-section of a solid tire.

are those least subject to fatigue rupture (at the center), and because of the complete absence of concentrations of forces on the surface.

CRITERIA TO BE OBSERVED IN THE DESIGN OF RUBBER ARTICLES SUBJECTED TO DYNAMIC STRESSES

In the studies by the author of rubber models placed between parallel glass plates, the deformations appear only in one plane; the profile of the model must be modified so that the material is not stretched along it. This procedure is possible only for models of compressed materials and evidently not for those subjected to tensile stress.

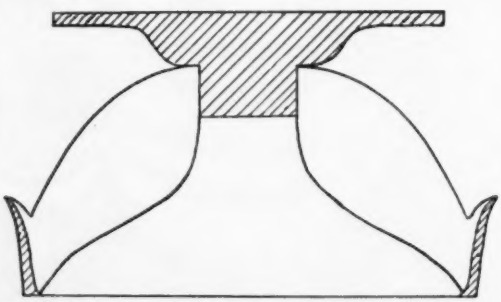


FIG. 25.—Modified cross-section of the shock absorber for trucks shown in Figure 7.

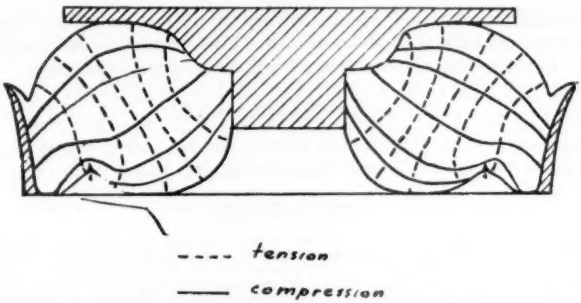


FIG. 26.—Isostatics of the model shown in Figure 25.

In the case of rubber specimens, the deformations occur in space; the isostatics tangent at every point of the surface are perpendicular to each other. The study of flat models may suggest such a shape that the material is compressed only along one of these two isostatics; along the other, there is generally tension, which must be kept within a very limited range of values.

This can be obtained by a suitable choice of cross-section for study with the model, and above all by experimentation.

CONCLUSIONS

In every case studied, rupture caused by fatigue begins at the stressed surfaces, i.e., conforms to tension isostatics tangent to the external profile, and then extends inward.

It is, therefore, necessary to restrict the deformations by surface tensile stresses within the narrowest possible limits.

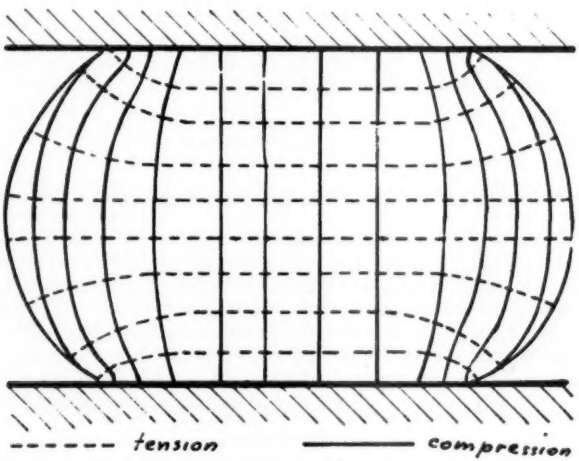


FIG. 27.—Isostatics of the cross-section shown in Figure 5.

The photoelastic method, even with very simple means, makes it possible to confirm experimentally the existence of local deformations, and facilitates the search for improvements in the fatigue resistance of rubber articles.

ACKNOWLEDGMENT

The author thanks Dr. Stefano Oberto for his valuable advice, and the Pirelli Società per Azione for permission to publish this article.

REFERENCES

[1] Van Geel and Eymers, *Rubber Age* (N. Y.) **29**, 491 (1929); Rowland, *Ind. Eng. Chem.* **22**, 1182 (1930); Thibodeau and McPherson, *J. Research Natl. Bur. Standards* **13**, 887 (1934); Treloar, RUBBER CHEM. & TECHNOL., **31**, 347 (1948); Treloar, *Rubber Age* (N. Y.) **63**, 195 (1948).
[2] Coker and Filon, "A Treatise on Photoelasticity", Cambridge University Press, London, **1931**; Mindlin, *J. Applied Physics* **10**, 222, 273 (1939); Le Boiteux and Boussard, "Élasticité et Photoelasticimétrie", Hermann & Cie., Paris, **1940**.
[3] Hurry and Chalmers, *India Rubber World* **119**, 717 (1949).
[4] Van Geel and Eymers, *Rubber Age* (N. Y.) **29**, 491 (1929).

DYNAMIC DAMPING AND YOUNG'S MODULUS IN THE RANGE OF RUBBERLIKE ELASTICITY *

R. ECKER

RUBBER AND SYNTHETICS DIVISION, FARBENFABRIKEN BAYER A.G., LEVERKUSEN, GERMANY

THEORETICAL CONSIDERATIONS

The principles of our present concepts of high elasticity (the idea of high elasticity was introduced into scientific literature for the first time by Houwink[1]) are the thermodynamic consequences of the kinetic theory of Meyer, von Susich and Valko[2], Kuhn[3], and Guth and Mark[4]. On the basis of these concepts, Scott[5] has formulated three postulates for the high elasticity of a material: (1) the substance must be macromolecular, that is, it must be composed of very long chain-molecules; (2) the polymer must possess inter-molecular cohesion so that the material is a three-dimensional network of such chain molecules; and (3) high elasticity results from the interplay between atomic vibrations and the intermolecular cohesive forces and, consequently, depends on the temperature.

The second and third postulates can be expressed mathematically on the basis of the theoretical considerations indicated. For the force necessary to produce a certain deformation and frequency of cross-links in the network, Treloar[6] derived the following relation:

$$K = NkT\left(m - \frac{1}{m^2}\right) = \frac{pRT}{M}\left(m - \frac{1}{m^2}\right) \tag{1}$$

Here K is the force required to stretch a cube of 1 cc. by m centimeters; N is the number of points of cross-linking per cc.; k is the Boltzmann constant, R is the gas constant; T is the absolute temperature; M is the molecular weight between adjacent points of cross-linking; and p is the density.

Wall[7] arrived at practically the same formula, in explaining the rupture of the valence bonds:

$$\sigma = NkT\left[\frac{\Delta l}{l} - \left(\frac{l}{\Delta l}\right)^2\right] \tag{1a}$$

that is, the value of the tensile stress is proportional to the number of molecular chains per unit volume.

Both equations indicate the same surprising fact; that high elasticity has no connection with the chemical constitution of high polymers, but is related to the geometrical shape of the macromolecular network and the frequency of linkages per unit volume. This concept has recently been verified strikingly by substances in which polyester molecules are united with diisocyanates (Vulcollan).

Scott's third postulate can be formulated mathematically in the best way by the equation established by Kuhn[8] on the basis of that of Maxwell[9] for the relaxation of elastic stress as a function of time:

$$\sigma = \sigma_0 \cdot e^{t/\tau} \tag{2}$$

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from *Kautschuk und Gummi*, Vol. 6, No. 7, pages WT 127–139, July 1953. This paper was presented at a meeting of the German Rubber Society in Goslar, May 7–9, 1953.

Here σ_0 is the stress at time $t = 0$; τ is a material constant which depends on the temperature, the "relaxation time", that is, the period in which the stress σ decreases to the eth fraction of its initial value[10] σ_0. Applying the elastic modulus (E), Kuhn established the following relation for a high elastic material:

$$E = E_0 \cdot e^{-t/\tau_0} + E_1 \cdot e^{-t/\tau_\infty} \qquad (2a)$$

Here he correlates the first term of the micro-Brownian movement and the second term of the macro-Brownian movement. This relation represents an abstraction of the actual situation, while the plastic-elastic behavior is reduced to two limiting relaxations. Actually, a continuous relaxation spectrum must be assumed. This simplified equation of Kuhn suffices in many cases, if it is kept in mind that it is an expedient abstraction.

Considering the relaxation time to be the quotient of the viscosity (η) and shear modulus (G): $\tau = \frac{1}{k} = \frac{\eta}{G}$, the plastic-elastic behavior of a high polymer can be best illustrated by equivalent mechanical or electrical models[11].

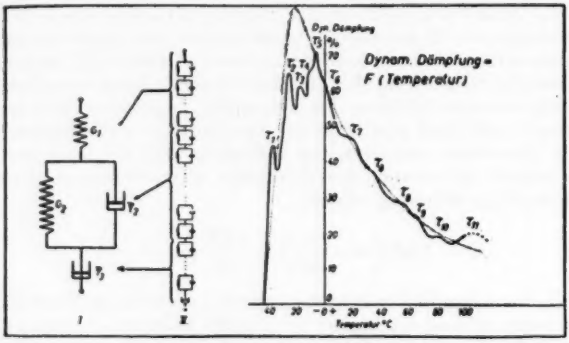


FIG. 1.—Model representation of a high polymer.

The model shown diagrammatically in Figure 1 (I) represents the relations in Equation 2a, and is a combination of the Maxwell and Voigt models, the latter often known as the Kelvin model[12]. By this electrical connection of both models in series, a mechanism of deformation is described, which comprises both inertialess elastic and also plastic and retarding elastic deformations. If these bodies undergo deformation (γ), this deformation is calculated from the individual amounts as follows:

$$\gamma = \frac{S}{G_1} + \frac{S}{G_2}(1 - e^{-t/\tau_2}) + \frac{S}{\eta_3} \cdot t \qquad (3)$$

where S is the shearing force and G_1 and G_2 are the shearing moduli.

However, if a whole relaxation spectrum is assumed, as is the case for practically all high polymers, Equation 3 is accordingly expanded to the integral form for (2) in Figure 1:

$$\gamma = S\left[\frac{1}{G_1} + \int \frac{1}{G}(1 - e^{-t/\tau})d\tau + \frac{1}{\eta_3} \cdot t\right] \qquad (3a)$$

The derivation of these mathematical formulas can be dispensed with here, since this has been done in detail in the literature quoted[13]. The curve in Figure 1 for the relative damping of a vulcanizate of Butyl rubber shows convincingly that model II represents the real mechanism. The dotted curve would be more in conformity with model I. It evidently represents a simplified generalization of the plotted curve obtained experimentally. The details of this experiment will be described in more detail later.

The experimental determination of the relaxation behavior of a high polymer can be made in various ways, namely, by static and dynamic methods. In the field of rubber elasticity, the relaxation times are of diminishing order of magnitude with respect to the experimental times. Hence it is preferable to make such measurements dynamically in order to arrive at a useful relation between experimental and relaxation times. The best defined are the experimental times of dynamic vibrations. These vibration experiments can be carried out in free as well as in forced systems. A number of authors have already described experimental results for rubber and synthetic materials. Free vibration was employed by Yerzley[14], Kuhn and Künzle[15], Jenckel[16], Schmieder and Wolf[17], Reiss[18], and others. In the field of forced vibrations, the extensive works of Roelig[19], Oberto and Palandri[20], as well as Kainradl and Händler[21] are particularly important.

With free vibration, the frequency of a vibration cycle and in most systems the amplitude as well, is determined by the structure of the material as well as by the experimental temperature. Schmieder and Wolf[17] determined the frequency relation by changing the torsional moment at constant weight of the oscillating disk by the torsion mechanism. In the determination of rebound resilience, rubber technology has for decades utilized the principle of free vibrations. The theoretical relations between rebound resilience and internal damping were first investigated by Stöcklin[10] and recently by Schreuer[22], and confirmed by experimental results. Free and damped vibration processes can be represented mathematically according to the differential equation:

$$a\ddot{x} + b\dot{x} + cx = 0$$

$$\left(a\frac{d^2x}{dt^2} + b\frac{dx}{dt} + cx = 0\right)$$

This formation is the basis of the theoretical derivations of most authors. However, in order to verify mathematically the relations given experimentally and in the model of Figure 1, it should be remembered that, in every high polymer, many more or less marked cohesion mechanisms are responsible for the plastic-elastic behavior. These cohesion mechanisms each form a system, per se, capable of vibrating, which, however, is coupled to the others in turn in some way. For a clear mathematical representation, it must be remembered that here we have a system of coupled vibrations. Klein and Jenckel[23] claculated such systems by coupling several Maxwell models.

In forced vibrations, a periodic force is exerted externally, by which the frequency and amplitude are also governed. The differential equation of these vibrations accordingly has the form:

$$a\ddot{x} + b\dot{x} + cx = P\cos\omega t$$

$$\left(a\frac{d^2x}{dt^2} + b\frac{dx}{dt} + cx = P\cos\omega t\right)$$

Naturally, here too, it is a question of one complete system of coupled vibrations. While in free damped vibrations, the internal damping of the testing materials can be determined most conveniently by means of the decrement, in forced damped vibrations, this property can be ascertained by means of a hysteresis-loop. This hysteresis-loop is then always an ellipse, if the resistance is proportional to motion of the deformation velocity in question. This, however, is always assumed to be true where Maxwell's exponential law, and also expansion, according to Kuhn, can be regarded as valid and definitive.

If P_ρ is the resistance of the system to motion, ρ the damping resistance, and V the velocity in question, then:

$$P_\rho = \rho \cdot v$$

If the distance for sinusoidal deformations is s:

$$s = a + a \sin (\omega t)$$

$$v = \frac{ds}{dt} = \omega \cdot a \cdot \cos (\omega t)$$

$$P_\rho = \rho \cdot a \cdot \omega \cdot \cos (\omega t)$$

By rotation in the coordinate axis:

$$x = a \cdot \sin (\omega t) = s$$

$$y = b \cdot \cos (\omega t) = P_\rho = \rho \cdot a \cdot \omega \cdot \cos (\omega t)$$

This is, however, the parameter representation of an ellipse[24]. From the inclination of the long ellipse axis to the long axis, by means of the tangent of the angle of inclination:

$$\tan (\omega t) = \frac{P}{s} \left[\frac{kg}{cm} \right]$$

the elastic constant and, by conversion to surface and length units, Young's modulus (in kg. per sq. cm.) can be determined. In the following experimental part, only the elastic constant will be adduced, because the dimensions of the test-specimens are the same in the comparative studies.

EXPERIMENTAL RESULTS

DAMPING EXPERIMENTS WITH INITIAL COMPRESSION

The experimental results recorded in Figure 2 were obtained in order to investigate the reinforcement problem of specific fillers by means of the dynamic vibration method, especially as developed and applied by Roelig. To this end, four different fillers were chosen, whose effects are sufficiently known to every rubber technologist from tests by the classic statistical methods; namely, a highly active channel carbon black, a highly active colloidal silicic acid, a semiactive channel carbon black, and an inactive filler. The study was made under a pressure of 11.5 kg. per sq. cm. and an alternating load of ± 6.15 kg. per sq. cm. and at a frequency of $16\frac{2}{3}$ Hz (that is, 1000 load changes per minute). In every case the measurements were made at temperatures from $-60°$ to $160°$ C. The filler loadings ranged from 0 to 50 per cent by volume. The damping values were, above 20° C, highest for the two highly active fillers, lowest for the inactive filler, and intermediate for the semiactive one. Below 0° C, no more essential differences in the effects of the different types of filler on rubber could

be established. Disregarding first of all colloidal silicic acid in the consideration of the dynamic elastic constant, no gradual differentiation of the inactive, semiactive, and highly active fillers is revealed by this test. On the other hand, the course of the curve of dynamic elasticity for active channel carbon black is quite different from that of colloidal silica; the values for the carbon blacks are considerably lower. This result is all the more surprising, since active channel carbon blacks in a static tension test (see Figure 3) show much higher stress values (moduli) than does active silicic acid. These relations are

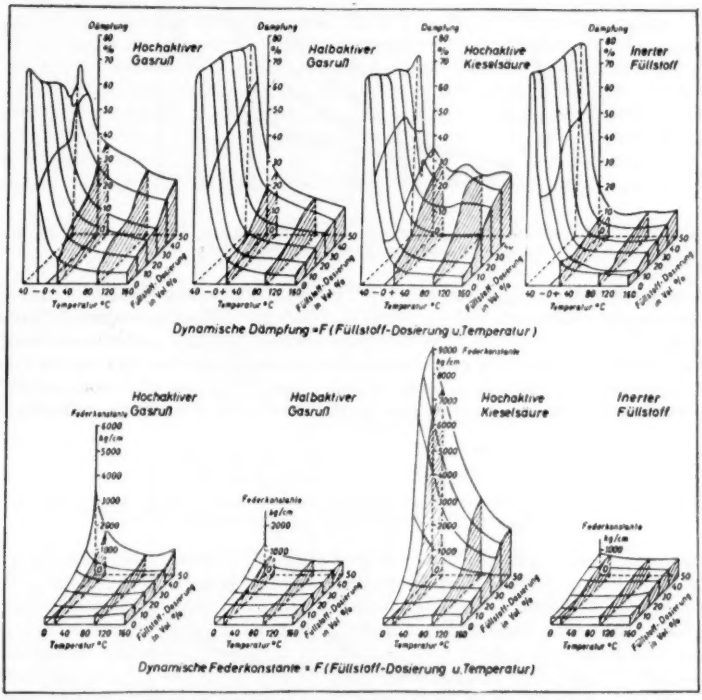


FIG. 2.—Dynamic properties of vulcanizates. The legend for the upper three-dimensional diagrams reads *Dynamic damping = F (filler concentration and temperature)*. The vertical axes represent *damping*, and from left to right show *highly active carbon black, semiactive carbon black, highly active silica*, and *inert filler*. The legend for the lower graphs reads *Dynamic elastic constant = F (filler concentration and temperature)*. The vertical axes represent *elastic constant* and from left to right are the same as the upper diagrams.

shown in greater detail in Figure 4, in which the relation between the static stress (σ_{300}) and the dynamic elasticity is plotted on a curve. On the curve for carbon black, the values of seven different carbon blacks are utilized. Despite the different activities of the seven blacks, all the experimental values lie on the same curve. Accordingly the blacks at high static stresses give low dynamic values of Young's moduli, while the silicic acids show high dynamic values of Young's moduli at low stresses. The relations between Shore hardness and dynamic elasticity are quite similar, although not so marked (see Figure 5).

This means that mixtures or vulcanizates containing silica under static stress have a weaker action than under dynamic stress (compression). An explanation of this important divergence can perhaps be found in the difference in the secondary agglomeration of the primary particles of both types of filler.

Carbon blacks have pronounced chain structures, which must be present in some form even after incorporation into rubber (see conducting blacks), while

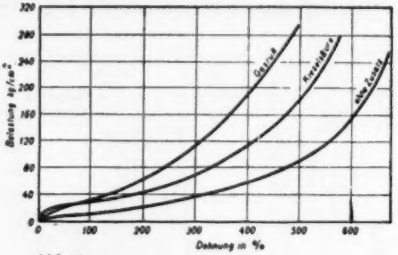


FIG. 3.—The abscissa represents *percentage elongation*, the ordinate the *load in kg. per sq. cm.* The curves are, in descending order, *carbon black*, *silica*, and *no filler*.

silica forms spongier agglomerates[25]. The chainlike carbon black agglomerates more readily conform to deformations to which the rubber is subjected than do the agglomerates of silica. Inactive fillers, whose primary particles are mostly of the order of magnitude of the secondary particles of silica, can not be taken as examples of the contrary, since in their case, separation of rubber and filler appears even at small deformations, so that the layer of rubber enveloping the

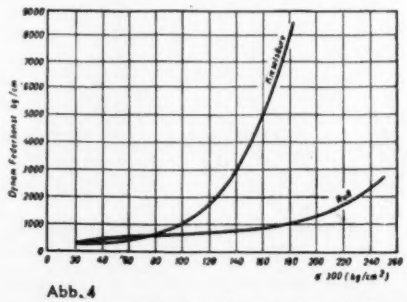


FIG. 4.—The abscissa represents σ_{300} (see text), the ordinate the *dynamic elastic constant in kg. per cm.* The upper curve is *silica*, the lower curve is *carbon black*.

filler particles becomes more mobile and thereby more easily deformed. If the elastic recovery forces in vibration experiments with initial compression are not within a definite order of magnitude, so that, even after a relatively short time of stress, especially at high temperatures, considerable permanent deformation appears, the phenomena relating to Young's modulus shown in Figure 6 are observed. This is observed with insufficient curing of rubber vulcanizates, with some vulcanized polymers which retain a pronounced degree of thermoplasticity, even after cross-linking, with some types of fillers, and when the formulation is

unsatisfactory. Even if this phenomenon has been shown to be true of alumina gel, it does not imply any adverse criticism of this filler, but only shows that erroneous conclusions can result by the use of an ill-chosen formulation. The increase of the elastic constant at higher temperatures is explained by the fact that the sample is so irreversibly deformed by the initial compression that it necessarily becomes harder.

DAMPING EXPERIMENTS WITH DIFFERENT COMPRESSIONS AND TENSIONS

Such erroneous interpretations, as illustrated here, can be avoided if the compression is reduced and one passes from compression to tensile stress. In order to make clear comparisons, the specimens were vulcanized on metal plates with Desmodur-R. For exact temperature control, it was necessary to vulcanize the cylindrical test-specimens (60 mm. diameter and 60 mm. height) partially by a series of metal disks. This necessarily introduced a series of uncontrolled boundary layers between rubber and metal, but since all the samples were prepared in the same way, this condition can be regarded as practically constant. The tests were made with a compression of 0.3 kg. per sq. cm. and a

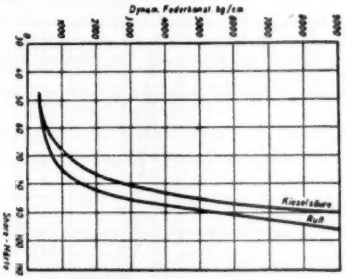


FIG. 5.—The abscissa represents *Shore hardness*, the ordinate the *dynamic elastic constant in kg. per cm.* The left-hand curve is *silica*, the right-hand curve is *carbon black*.

stress of 6.0 kg. per sq. cm. The mixtures were of the same composition except for the filler and the active agents which were then necessary. With the exception of the CK-3 mixture, the dynamic damping is lowest above 20° C at an initial tension of zero kg., while no noteworthy difference is observed between compression and tensile stress. The vulcanizate containing CK-3 had the highest damping value, followed by the vulcanizates containing Vulkasil-S, Durex-O, Albafix, and finally the vulcanizate containing no filler. Although damping values of zero per cent are plotted for the latter, it must be realized that, strictly speaking this is in reality never observed, since, according to all theoretical considerations, some damping must always appear. Where a damping value of zero is recorded in our experiments, the order of magnitude is to be regarded as so small that the dynamometer does not show these small quantities precisely. For Young's modulus and the elastic constant, the CK-3 mixture again is an exception. While for all other vulcanizates, Young's modulus is greatest at the highest compressions in all temperature ranges, and also becomes smaller in the transition from compression to tension, it increases for the CK-3 mixture from an initial compression of 6 kg. per sq. cm. to lower compressions, reaches its maximum at an initial load of zero kg. per sq. cm., and falls with increasing initial tensile stress, as do the other vulcanizates.

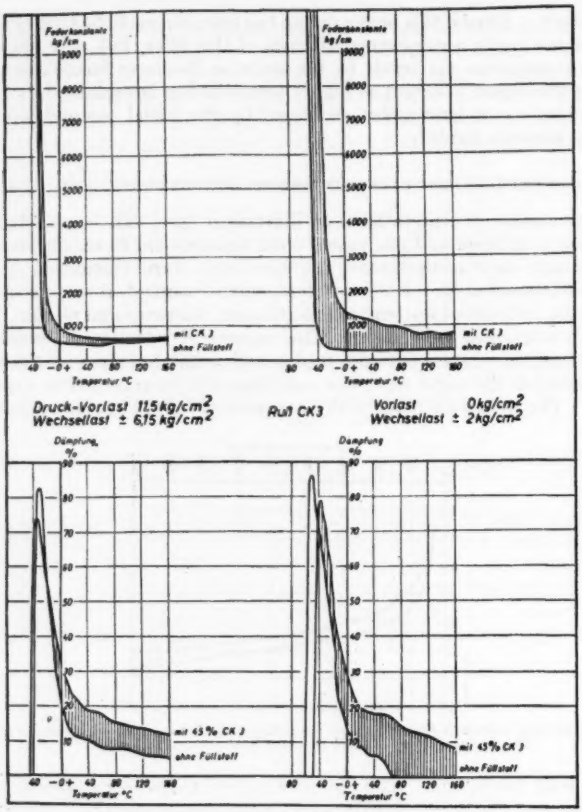


FIG. 6.—The legend in the center of the figure reads:

Initial load 11.5 kg. per sq. cm. *Initial load 0. kg. per sq. cm.*

CK3 Carbon black

Alternating load ±6.15 kg. per sq. cm. *Alternating load 2 kg. per sq. cm.*

The ordinate of the upper diagrams represents the *elastic constant*, that of the lower diagrams *damping*. In the upper diagrams the upper curve is *CK3 carbon black*, the lower curve is *no filler*. In the lower diagrams, the upper curve is *45% CK3 carbon black*, the lower curve is *no filler*.

Morrison[26] studied the behavior of rubber under compression and tension, though only at static stresses. He proved that the elongation curve and the compression curve have an identical course, if the actual and not the initial cross-section is used as a basis. In studies of carbon black, the stiffening is just as evident by the compression curve as it is by the stress-strain curve. In an attempt to eliminate the influence of carbon black in the mixture and relate the compressibility to the rubber alone. Morrison found that the calculated curves did not coincide with the experimentally found curves of carbon black-free mixtures, but had very irregular courses. We thus are dealing with an irregu-

lar behavior of the vulcanizates containing carbon black in both dynamic and static compression-tension investigations. This phenomenon will not be explained in detail here, since it will be understood more easily on the basis of later considerations.

In Figure 6 the influence of various fillers on the dynamic properties (damping and Young's modulus) of the vulcanizate[27] is recorded. Loaded mixtures are compared with unloaded mixtures; the shaded area represents the influence of the filler. The fillers were chosen so that the static tension-curves proceed approximately equidistant, that is, the stress values (σ_{300} or σ_{400}) differ by roughly equal amounts. The mixture containing no filler naturally has the lowest stress value, followed in order of increasing modulus by the mixtures containing Albafix, Durex-O, and Vulkasil-S. If we take the static modulus as a measure of the reinforcing action of a filler, it is possible to come to an erroneous conclusion, since colloidal silicic acids could then be regarded as only semi-active fillers. However, if the shaded areas of Figure 6 are considered, and the changes of dynamic values by the fillers CK-3 and Vulkasil-S are compared, it is obvious that the two fillers are equally active. In Equations 1 and 1a, it was shown that every deformation of a high-polymer substance, in the present case vulcanized rubber, leads to the dissolution of certain valence bonds. This is also to be assumed in vibration experiments. Every damping measurement is an energy measurement; thus the shaded areas are a measure of the energy of union between rubber and filler. The energy relations, and the three possible types of bonds which can be broken in such deformation processes, have been explained in greater detail by Houwink[28].

Accordingly, the changes of internal energy dU can be divided in two phases:

$$dU = U_{PF} + (U_{PP} + U_{FF})$$

Which of the three types of bonds, P↔F, P↔P, or F↔F (P = polymer, F = filler) are broken by these deformations depends in part on the cohesion relations of the filler and the adhesion mechanism between the high polymer and the filler.

A second very important phenomenon is indicated by Figure 6: in pure compression (11.5 kg. per sq. cm. initial compressing load and ±6.15 kg. per sq. cm. alternating load), the distinction between unloaded vulcanized rubber and loaded mixtures in both damping and in the Young's modulus, or the elastic constant, is considerably smaller than in oscillation about the zero position, that is, with an initial load of zero kg. per sq. cm. and a tension or compression of, e.g., 2 kg. per sq. cm. If the vibration tests are carried out only under initial compressing and alternating loads, it is possible that, for some inactive fillers, lower damping and elasticity values will be found than for the unloaded mixture. Such a result is difficult to understand and contradicts every experience of rubber technology. These experimental results justify the assumption that, in pure initial tensile and subsequent alternating stresses, still greater differences are to be expected.

DAMPING EXPERIMENTS UNDER TENSILE STRESS

For this experiment a special apparatus was developed, which is shown schematically in Figure 7 and in detail in the photograph in Figure 10. The apparatus consists essentially of a motor with an adjustable eccentric, a mechanism for controlling straight-line motion, a mechanism for initial stressing, with different clamps to hold the stretched test-specimens at the desired elongation.

The test-specimen itself is the ring R III, which, after removal of ring R I and Ring II, serves for any static tensile and tear resistance tests which may be desired.

The initial-stress mechanism with the test-specimen is enclosed in a housing for tempering. The latter is in turn connected with a cold- or heat-control, so that all the investigations can be undertaken at low as well as at high temperatures. The small-sized specimen has the advantage that it can also be taken from small samples of material and can be uniformly tempered more easily. Force (a dynamometer) and distance indicators are coupled by a system of mirrors, so that the hysteresis loops are thrown optically on a screen and can be recorded there. The experimental temperature is read on a voltmeter directly on the specimen, with a heat element. By means of the adjustable eccentric, the amplitude can be varied. In the experiments to be described below, the amplitudes varied from 2 to 3 per cent; therefore they were kept very low. The influence of different amplitudes, as was reported by Oberto and Palandri[20], and by Gui, Wilkinson and Gehman[29], has not yet been studied in detail with our present apparatus. The influence in any case is not very great,

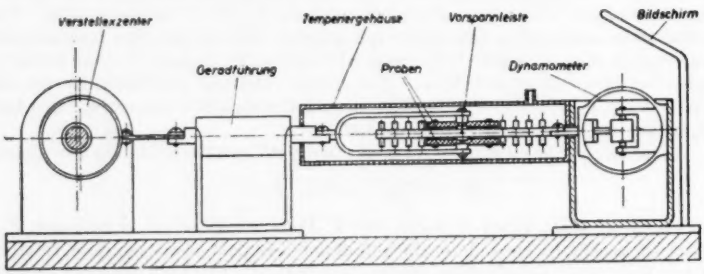


FIG. 7.—Diagrammatic scheme of the damping machine for tensile stress measurements.

and variations of the order of magnitude of 1 to 5 per cent hardly influence the test results. In the present system, we are in a position to obtain measurements at three different frequencies, namely, at 8⅓, 16⅔ and 25 Hz. There is no mechanical obstacle to setting up a frequency of 50 Hz. At these frequencies, no great displacement of the damping maximum nor change in Young's modulus is observed as one passes from one of the frequencies indicated to another. This occurs only if the frequency difference is of the order of magnitude of decimal powers. However, as has been shown many times in the literature, a sufficient parallelism between frequency and temperature relations exists, so that the dispersion range is displaced toward higher temperatures with rising frequency; in our opinion it is sufficient to make measurements at one frequency which is easily controlled by the apparatus, and to vary the temperature. The smaller the dimensions of the specimen, the easier and more precise is control of the temperature.

The first experiments with this mechanism were made with the same mixtures that were tested in the experiments shown in Figure 6. Even the unloaded mixtures show surprising results. The freezing point, that is, the transition to so-called steellike elasticity, is displaced to lower temperatures at higher initial stresses. That damping at temperatures above 0° C with increasing initial elongation becomes better, i.e., lower, is to be expected; but it is difficult

to understand the decrease of Young's modulus with increase of initial elongation in all temperature ranges. This is most evident at temperatures below 0° C, e.g., in the range of −40° to −50° C it at first decreases, i.e., up to elongations of 100 to 140 per cent, and only at 220 per cent regains the value it had at 20 per cent elongation. If we, like Kuhn[3], assume that in converting a piece of rubber from the unstretched to the stretched state, the loosely coiled molecules in the static stage change in length, width, and thickness, and thereby become oriented, and that the elastic stress in stretched rubber corresponds to a tendency to return from an improbable to a probable state, then this experimental result stands in apparent contradiction. According to this, by stretching up to 140 per cent, at first only a probable state would be created. We believe that these phenomena can only be interpreted thus: that, by stretching to 140 per cent, the separation of some valence bonds is superimposed on the orientation processes, which predominate only above this degree of stretching. This, however, touches the question of the union of sulfur with the rubber molecule. If the sulfur were bound to the rubber in vulcanization only by primary valences, the experimental results would still be difficult to explain. It must, therefore, be assumed that the associations at the point of cross-linking, to which those formed by sulfur during vulcanization also belong, must be, in part, of a lower order of magnitude, so that these slight forces, as they appear on stretching to 100 per cent and at 140° C, suffice to explain certain of the bonding mechanisms. By further stretching, i.e., beyond 140 per cent, the orientation process prevails, and then certain stiffening phenomena appear, which are evident by crystallization processes. Whether the intermolecular forces which develop during vulcanization through the association of sulfur and rubber are primary or secondary valences can not be discerned from this experiment, especially because these forces are often transitory, since, in an intermolecular reaction, the primary valence bonds of the reacting groups, are also more or less involved[30].

The thermodymic relations in deformed rubber have been set forth by Houwink[31]. According to him, the following equation is valid for a deformed system:

$$\sigma = \left(\frac{\delta U}{\delta l}\right)_T - T\left(\frac{\delta S}{\delta l}\right)_T$$

where σ is the tension, U the internal energy, S the entropy and T the absolute temperature.

Hitherto two border cases have been distinguished:

(1) $$\frac{\delta S}{\delta l} = 0$$

the steel-like elasticity without change of entropy; then

$$\sigma = \left(\frac{\delta U}{\delta l}\right)_T$$

and

(2) $$\frac{\delta U}{\delta l} = 0; \quad \text{then } \sigma = -T\left(\frac{\delta S}{\delta l}\right)_T$$

and these relations are valid for high elasticity. These relations are strictly applicable only to pure unvulcanized rubber subjected to static deformation

stresses. However, even in an unloaded vulcanizate, the change of potential energy is equal to zero up to a certain elongation, because a positive and a negative effect neutralize each other. In a broader range with higher elongations (in our case also in the passage from the minimum to the maximum Young's modulus) $\frac{\delta U}{\delta l} < 0$, that is, it is negative. This is the range of incipient (quasi) crystallization, and only beyond this second range is $\frac{\delta U}{\delta l} > 0$, that it, it is positive, and the material again behaves elastically like a metal.

The mixture loaded with active carbon black (CK-3) has, as was the case in experiments described earlier, higher damping values than the unloaded mixture. The highest damping values are reached in the range of elongations in which the elastic constant reaches the lowest value. Here, too, the Young's modulus values are reduced by preliminary stretching. Stretching to the point where the value of Young's modulus is a minimum is in any case considerably lower (60 to 100 per cent) than for the unloaded mixture. Therefore the quasi-crystalline region is much more pronounced. This phenomenon is related to the problem of reinforcement by active fillers. It appears that the layer of rubber enveloping the filler particle is already under permanent tension and therefore is already oriented. Houwink[28] constructs his theory of "overstressed" molecules on this assumption.

Among further experiments, the mixture containing active silicic acid (Vulkasil-S) deserves a particular explanation. At small stresses, the damping and elastic values of the mixture containing silicic acid are little different from those of the mixture containing active carbon black. At higher elongations, however, the differences become very considerable. Now the dynamic Young's moduli of the vulcanizates containing silicic acid under tensile stress are lower than those of mixtures containing active carbon black, i.e., the relations are the opposite of those found for compression (see Figure 2). The explanation given there of the easier orientation of the chainlike secondary agglomerates should apply here, too. This must also be the reason for the considerably higher elasticity values for the semiactive carbon black, Durex-O, for initial elongations over 140 per cent. Although the primary particles of this carbon black have a diameter almost ten times higher than that of Vulkasil-S, it has a higher elasticity value than the latter. However, this carbon black also has a pronounced chain structure, and therefore is more easily oriented in the rubber during the stretching process. The slightly active filler Albafix has the lowest values of both damping and elastic constant.

All previous studies have been made with vulcanizates of natural rubber. In the results to be described, nearly all the materials were synthetic high polymers. Three butadiene-acrylonitrile emulsions in which the proportions of butadiene and acrylonitrile were approximately the same, i.e., 32–34 to 68–66, were compared. Even if no notable differences were found in the damping values, great differences were found in the elastic constants. First an essentially different value of Young's modulus was observed in contrast to the value for the almost identical natural-rubber mixture. The slight tendency to crystallize with increasing elongation is particularly striking in the first two polymers. This indicates a different, i.e., a more tightly coiled structure of the macromolecule, in which parallel alignment of the molecules or segments of molecules can hardly take place during the orientation processes. This appears rather to be the case of Polymer III. Each of the three mixed polymers was prepared by a different polymerization process. The most important experi-

mental data, such as tensile strength, elongation at rupture, hardness, swelling, etc., may be regarded as the same for the three polymers. In dynamic testing with preorientation, however, complicating differences appear. The polymerization method used for polymer III gives a product having a less coiled molecular structure, which is more like that present in natural rubber.

Experiments were also made with Neoprene-W. The reinforcing action of carbon black, when compared with an unloaded mixture, was evident. The crystallization phenomena are here just as evident as in natural rubber. In other mixtures studied, the change of mechanical and elastic properties brought about by the addition of 0.5 per cent of an accelerator was evident. The effect of these additional ingredients was such that not only is the network-forming reaction accelerated, but the general properties of the vulcanizates are modified. The vulcanizates become more resistant to cold, and possess better damping properties at higher temperatures, i.e., higher elasticity. At the same time the dynamic tensile strength at elevated temperatures is recorded in these experiments. It is known that this modification is most clearly seen in Neoprene-W. Studies of other types of Neoprene have not yet been concluded.

A similar modifying action on the general properties is observed with suitable activators for a number of light-colored reinforcing fillers[32]. Natural-rubber mixtures containing alumina gel (Teg) were investigated. One mixture contained no filler activator, while the others contained 5 per cent Akticit-A, based on the filler content. By the addition of Akticit-A, the damping, especially at elongations up to 140 per cent, was reduced considerably, and the elastic constant was increased in all the elongation ranges. As for the elastic constant, the mixture containing no Akticit acts like one containing an inactive filler, while only in the second mixture does Teg exhibit its active properties.

Vulcanizates of Polysar-Butyl 200 (see Figure 9) show an extremely irregular damping curve for all the mixtures. Each of the damping curves obtained has a series of pronounced damping maxima (see also Figure 1), so that one must assume that, in this polymer, several heterogeneous binding mechanisms are present together, all of which however are "coupled" with each other in some way. These series of bond mechanisms are also clearly observed in the elastic constant. The highest damping values were found with CK-3 carbon black and Vulkasil-S. Luv-36 and Vulkasil-C give lower damping values, especially at elongations above 20 per cent. The Young's modulus is increased most by CK-3. With both silicates, dynamically softer vulcanizates are obtained.

The plastic-elastic behavior of Vulkollan under dynamic stress was studied with soft and hard molded specimens, as well as with a kneaded condensate. In all these cases we have a polyester of pronounced linear structure, which is cross-linked with 1,5-naphthylene diisocyanate (Desmodur N-15). The polyadduction reaction of this high elastic product was studied by Bayer and collaborators and reported at various times[33]. In soft molded Vulkollan samples, all tests were made with the same sample. The first test was made approximately three days after preparation. The second test was made after about three weeks of storage, in which case the specimen sheet was again inserted in a frame of 0.5 mm. lower height and compressed for 10 minutes at 160° C. By this aftertreatment in the press, the elastic constant increased sharply above 30° C, so that one may assume that a preorientation took place during pressing. With slight preliminary stretching (20 per cent), Young's modulus at all temperatures, especially above room temperature, is unusually high compared with its value at the same temperatures at greater degrees of initial stretching. After completion of the reaction, the molecular mobility of this product appears

to be arrested and becomes free again only through a definite orientation (elongations of 60 per cent and greater). The suggestion of thixotropic phenomena is very obvious. In the more highly cross-linked hard molded product, this phenomenon is not so pronounced, although Young's modulus at elongations of 60 per cent and greater, particularly at temperatures of 20° C to 100° C, is lower than at 20 per cent elongation. These materials have a strong tendency to crystallize at elongations between 60 and 100 per cent. The kneaded condensate, which was masticated before final molding in the press, does not show these thixotropic phenomena. The whole three-dimensional representation of the properties, as reflected by the elastic constant, resembles very closely that of a natural-rubber vulcanizate containing active carbon black. If the highly adsorptive carbon-black particles are regarded as a means of separating

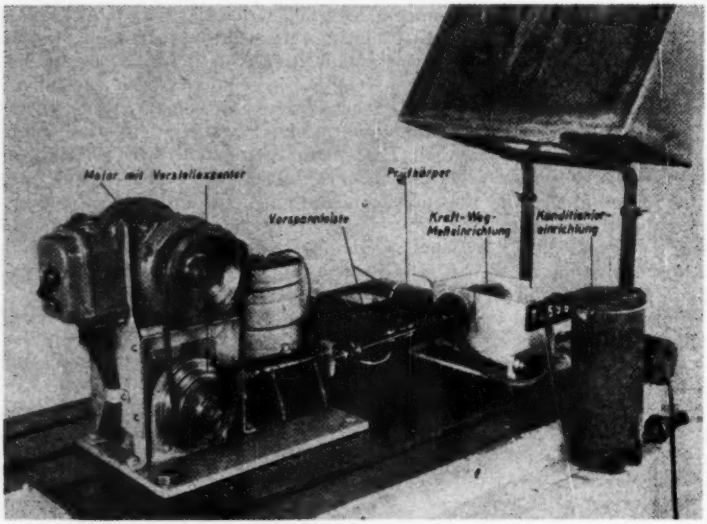


FIG. 8.—The damping machine shown diagrammatically in Fig. 7.

the chains of rubber molecules, as Bayer assumes for the loose-structure diisocyanate of the type of 1,5-naphthylene diioscyanate, this parallel behavior is understandable.

The forms in the three-dimensional representation of the Young's modulus are very instructive. The more pronounced is the second Young's modulus branch, the greater is the tendency of high polymers to crystallize, and the greater is their resistance to tearing. Vulkollan has the most pronounced second Young's modulus branch and also, as is known, the highest structural strength[34], or highest resistance to further tearing, highest impact resistance, and other characteristics. With this kind of test, a number of properties can also be ascertained, such as dynamic strength, heat resistance, elastic behavior, hardness, structural strength, etc.

In all the experimental results previously described, the hysteresis loops obtained were more or less marked ellipses, as would be expected on the basis

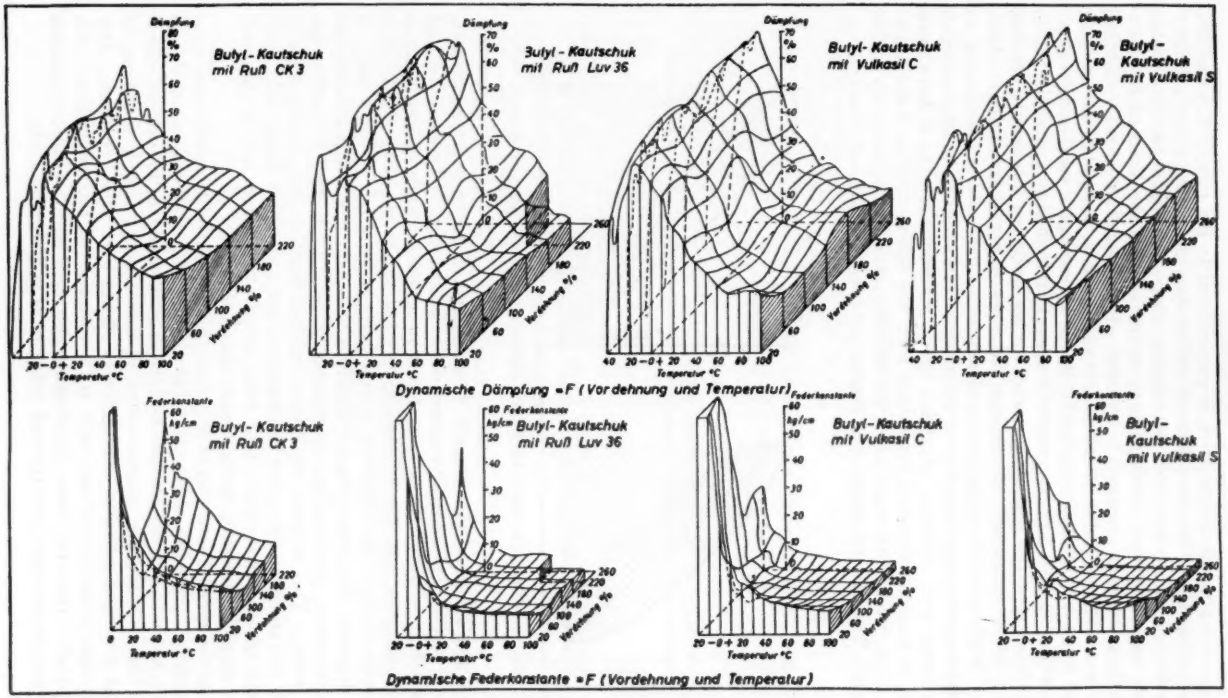


FIG. 9.—The legend for the upper diagrams reads: *Dynamic damping* = *F* (*Initial elongation and temperature*). The vertical axis of the upper diagrams is *Damping*, that of the lower diagrams is the *Elastic, constant*. In all diagrams the horizontal axes represent the *Temperature* and *Percentage initial elongation* respectively. All diagrams represent measurements of *Butyl rubber* vulcanizates. The upper and lower sets of four diagrams are *CKS carbon black*, *Luv-36 carbon black*, *Vulkasil-C*, and *Vulkasil-S*.

that the resistance to deformation is proportional to the rate of deformation. The experiments on the three Silicone-rubber specimens show a marked divergence of the hystersis loop from the elliptical shape (see Figure 10, II). As has already been discussed, an ellipse is an indication that the Maxwell-Kuhn exponential law can be presumed to be valid. If the deviation from the elliptical shape is so marked, it can be assumed that relaxation does not follow an exponential course. For such structural systems, Kubat[35] gave another derivation. Müller[36] has discussed the deviation of relaxation from the exponential course on the basis that the activating energy for the deviation mechanism depends on the initial structure. Deviations are more frequent for stronger structures. While hitherto nonexponential relaxation has been ascribed solely to relaxation spectra, and therefore to the presence of a series of different cohesion mechanisms with different relaxation times, we were not able, in our experiments, to find any essential divergence from the elliptical form of the hysteresis loops, even with relatively great preorientation (elongations up to 260 per cent). The only exception was Silicone rubber, as mentioned above.

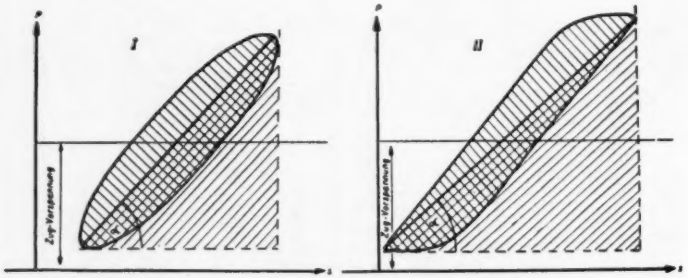


FIG. 10.—Diagram hysteresis loops. The abscissa represents the initial tensile stress.

The dependence of the dynamic damping and elastic constant on the temperature of the Silicone-rubber specimens is noteworthy. While all the high elastic polymers previously investigated show a quite broad temperature range in the transition from the rubber-elastic state to the steel-like elastic state (dispersion region), the transition here is fairly sudden, i.e., within a range of a few degrees. Both damping and elasticity values are practically independent of temperature. Our studies, not reproduced here, up to 200° C confirm this even better. This property of Silicone rubber, together with its capacity to absorb vibrations and its good resistance to fats and motor fuels, make it an excellent material everywhere that wide temperature ranges are encountered, as, for example, in elastic motor suspensions, etc.

That the effect of softening of polyvinyl chloride can be explained most comprehensively by studies of vibration has already been stated by a number of authors, so that a lengthy discussion of the experimental results is almost superfluous here. A broader interpretation of these results would, therefore, be possible if several softeners with different effects were tested together. Our experiments were carried out only with variation of the proportions with Palatinol-C. However, these experiments also show how the softener changes the elastic, mechanical, and thermal behavior of polyvinyl chloride.

SUMMARY

After a brief interpretation of current theoretical concepts of the high elasticity of macromolecular substances, as they have been developed by a number of authors from the laws of thermodynamics, the most important experimental methods of dynamic vibration are pointed out. A newly developed apparatus, which permits the study of the plastic-elastic behavior of high polymers in the rubber-elastic field by means of forced vibrations under tensile stress is described. With a plentiful supply of experimental material, various factors were studied, including the crystallization behavior of polymers, the reinforcing effect of various fillers, polymerization influences, modification of Neoprene-W by accelerators, the elastic behavior of Butyl and Silicone rubber, the influence of certain activators on the reinforcing properties of alumina gel, and the action of softeners in polyvinyl chloride.

REFERENCES

[1] Houwink, *Trans. Faraday Soc.* **32**, 122 (1936); *Kolloid-Z.* **77**, 183 (1936).
[2] Meyer, von Susich and Valko, *Kolloid-Z.* **59**, 208 (1932).
[3] Kuhn, *Kolloid-Z.* **68**, 2 (1934); **76**, 258 (1936).
[4] Guth and Mark, Mh. Chem. **65**, 93 (1934).
[5] Scott, *Trans. Inst. Rubber Ind.* **23**, 134 (1947).
[6] Treloar, *Repts. Progr. Physics* **9**, 113 (1943); Brit. Rubber Producers' Research Assocn., Publication No. **47**.
[7] Wall, *J. Chem. Physics* **10**, 485 (1942); RUBBER CHEM. & TECHNOL. **15**, 806 (1942).
[8] Kuhn, *Angew. Chem.* **52**, 289 (1939).
[9] Maxwell, *Phil. Mag.* [IV], **35**, 134 (1867).
[10] Stöcklin, *Kautschuk* **18**, 151 (1942); **19**, 3 (1943).
[11] Scheele, *Kautschuk u. Gummi*, **4**, 282, 447 (1951).
[12] Alfrey, "Mechanical Behavior of High Polymers", New York and London, **1948**; Scheele, *Kautschuk u. Gummi* **5**, 81, 104, 124 (1952).
[13] Wolf, *Kunststoffe* **41**, 89 (1951).
[14] Yersley, *Ind. Eng. Chem. Anal. Ed.* **9**, 392 (1937).
[15] Kuhn and Könale, *Helv. Chim. Acta* **30**, 839 (1947).
[16] Jenckel, *Kunststoffe* **40**, 98 (1950).
[17] Schmieder and Wolf, *Kolloid-Z.* **127**, 65 (1952).
[18] Reiss, *Kautschuk* **20**, 3 (1944).
[19] Roelig, *Kautschuk* **15**, 7, 32 (1939); *Kunststoffe* **30**, 164 (1940); *Gummi-Z. u. Kautschuk* **19**, 47 (1943); *Z. Ver. deut. Ing.* **87**, 347 (1943); Roelig and Heidemann, *Kunststoffe* **38**, 125 (1948); Fromandi and Roelig, *Kunststoffe* **38**, 245 (1948).
[20] Oberto and Palandri, *Rubber Age* (N. Y.) **63**, 725 (1948).
[21] Kainradl and Händler, *Kautschuk u. Gummi* **5**, 3, 22, 38 (1952).
[22] Schreuer, *Kolloid-Z.* **129**, 123 (1952).
[23] Klein and Jenckel, *Z. Naturforsch.* **7a**, 305 (1952).
[24] Lehr, "Schwingungstechnik", Verlag Springer, Berlin and Leipzig.
[25] Ecker, *Kautschuk u. Gummi* **5**, WT 171 (1952).
[26] Morrison, *Trans. Inst. Rubber Ind.* **12**, 426 (1937).
[27] Fromandi and Roelig, *Kunststoffe* **38**, 245 (1948); Fromandi and Ecker, *Kautschuk u. Gummi* **5**, WT 191 (1952); **6**, WT 6 (1953).
[28] Houwink, *Kautschuk u. Gummi* **5**, WT 65 (1952).
[29] Gui, Wilkinson, Jr., and Gehman, *Ind. Eng. Chem.* **44**, 720 (1952).
[30] Briegleb, in Freksa, Rajewsky and Schön, "Zwischenmolekulare Krafte", Verlag G. Braun, Karlsruhe, **1949**.
[31] Houwink, *Angew. Chem.* **65**, 84 (abstract of a paper) (1953).
[32] Ecker, "Die Dispergierung von Füllstoffen in Kautschuk", Report to the Deutsche Kautschuk Gesellschaft, in Goslar, May 7–9, 1953.
[33] Bayer, Müller, Petersen, Piepenbrink, and Windemuth, *Angew. Chem.* **62**, 57 (1950).
[34] Ecker, *Kautschuk u. Gummi* **5**, WT 49 (1952).
[35] Kubat, *Kolloid-Z.* **129**, 73 (1953).
[36] Muller, "Diskussions-Anmerkung zu I. Kabat", p. 35.

APPLIED FORCE AND SECOND ORDER TRANSITIONS OF RUBBER *

F. T. WALL AND DONALD G. MILLER

NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS

INTRODUCTION

Second-order transitions, which appear to mark the change from brittleness to elasticity, are well known for rubber[1] and numerous other polymers. The temperature at which such a transition occurs depends, among other things, on the kind of polymer, on the additives that are in it, and on how much it is cross-linked. It would also appear reasonable to expect that the second-order transition temperature would depend on the deformation of the sample, such as the elongation of a rubber strip. Accordingly, the research here reported was undertaken to investigate the effect of tension on rubber, in particular on rubbers with different degrees of cross-linking. The effect of such deformations might well provide further evidence regarding the nature of the phenomenon itself.

Three different cures of natural rubber were used for comparing cross-linking effects. In addition, a sample of GR-S and a sample of rubber reinforced with carbon black were included for comparison.

A decrease of T_m, the transition temperature, was found for these polymers when they were subjected to elongation. This problem has also been investigated previously for other polymers, a decrease in T_m likewise having been observed.

The determination of the transition temperatures was carried out by observing the length of a strip as a function of the temperature; the break observed in the slope of the length vs. temperature curve was taken to mark the transition point. The results will be discussed on the basis that transitions are caused by the onset of segmental rotations with particular reference to the effect of cross-linking and forces of extension. The effects of swelling agents on T_m will also be discussed briefly.

EXPERIMENTAL

The dilatometer arrangements ordinarily used for transition-point measurements are unsuitable for stretching experiments. The method which we used is similar to that of Müller[2], and was carried out as follows. The strip under tension was placed in a dry ice-acetone bath, which could be warmed up in stages. At each stage the length (or more accurately the change of length) of the strip was measured with a cathetometer. T_m is then taken as that temperature where the L vs. T curve takes a sharp change of direction. The process must, of course, be repeated for several different applied forces to provide data on the effect of force on T_m.

* Reprinted from the *Journal of Polymer Science*, Vol. 13, Issue No. 168, pages 157–164, Feburary 1954. The work was performed as part of the research project sponsored by the Reconstruction Finance Corporation, Office of Synthetic Rubber, in connection with the Government Synthetic Rubber Program.

The apparatus consisted of a rigid support which held a clamp for the strip. On the other end of the strip was another clamp attached to a cord, which in turn passed over two pulleys, and was then tied to weights. The sample, support rod, and clamps were submerged in a dewar containing an acetone bath which had previously been cooled to about −80° C with dry ice. The bath was stirred with a propeller stirrer, and was heated at the desired rate with an ordinary knife heater, controlled by a Variac. Acetone was used because it is a poor swelling agent for rubber.

The temperature was measured with a copper-constantan thermocouple, with the reference junction at 0° C. The e.m.f. was determined with a thermocouple potentiometer, which could be read to the equivalent of one-half degree.

A cathetometer, which was read to 0.05 mm., was placed approximately eight feet from the rest of the apparatus, and the change of length was followed by measuring the distance between a point on the cord and a fixed reference point. The measured distance was not the actual change of length because the clamps and clamp support also change dimensions with temperature, but, since these metals have no transitions in the region of interest, any change of the slope of the L vs. T curves is attributable to a transition of the polymer. A reference point was established to take care of instances when the cathetometer might be inadvertently moved.

An experimental run was carried out as follows. A strip was stretched under the desired force (f) between the two clamps in air at room temperature for 20 minutes to permit attainment of equilibrium. It was then submerged, still under tension, in the cooling bath which had previously been brought to about −80° C. An additional 20 minutes was then allowed for the strip to come to temperature equilibrium, and the length between the cord and reference point was recorded. The temperature was raised two to four degrees, seven minutes was allowed for coming to the new equilibrium, the temperature was read to the nearest degree, and the new length between the two points was recorded. The last process was repeated until data sufficient to determine T_m had been collected.

To verify that the T_m determined from tension experiments was not associated with a phenomenon different from that of the ordinary (i.e., without tension) transition temperature, it was necessary to compare the ordinary T_m with the value obtained by extrapolation to zero force of our T_m vs. f curves.

The ordinary T_m values were determined with an old dilatometer previously used in this laboratory. The apparatus consisted of a vessel connected to a capillary tube, mounted on a meter stick. This vessel, filled with polymer and a confining liquid, was likewise submerged in a cooling bath at −80° C. Thirty minutes was allowed for temperature equilibrium, after which the height of the meniscus of the confining liquid (acetone plus a dye) in the capillary was read from the meter stick. The temperature of the bath was raised three to five degrees, ten minutes was allowed for contents of the vessel to come to equilibrium with the bath, and the position of the meniscus was read again. This process was repeated until data sufficient to determine the transition point were collected.

Since the capillary was out of the cooling bath, fluctuations of room temperature affected the position of the meniscus, but fairly good results were obtained.

The polymers used[3] were 30, 60, and 90 minute cures of natural rubber without carbon black (labeled NR-30, NR-60, NR-90), a tread stock containing carbon black (labeled 40-N), and a sample of 30-minute cure GR-S. The di-

TABLE I

T_m (IN NEGATIVE DEGREES C) VS. STRETCHING FORCE FOR VARIOUS POLYMERS

	Force in grams										
Sample	199	399	599	699	782	899	1199	1399	1699	2199	2698
NR-30	—	63.5	65	—	—	67.5	—	69	—	—	—
NR-60	60	—	—	62.5	—	—	64	—	66	68	—
NR-90	59	—	—	60	—	—	61	—	62	63	—
40-N	—	—	—	—	60.5	—	—	—	63	—	65.5
GRS-30	56.5	—	—	57	—	—	58.5	—	59	59.5	—

mensions of the unstretched strips were 0.15 cm. thick and 0.6 cm. wide; the lengths ranged from 5 to 12 cm. The shorter samples were used with the larger forces so that the entire extended strip remained inside the dewar.

To obtain T_m from the results of a tension run, the differences (in cm.) of the readings of the reference point and the point on the cord were plotted against the temperature. The resulting curve had a break, the exact point of which was T_m. This point was determined fairly well by the intersection of the lines obtained by extrapolation of the other portions of the curve.

Below T_m, the points were generally on a straight line. Above T_m, some of the curves were straight, others slightly S-shaped. In the dilatometer runs, T_m was found by extrapolations from plots of the height of the meniscus vs. temperature.

Some runs were carried out under nonequilibrium conditions; that is, the strip was immersed in the coolant and the weights were applied afterwards. For these, the behavior of the points below T_m was similar to that of the equilibrium runs. Above T_m, however, the curves were much steeper and exhibited a marked S-shape. Since such results were unreproducible, this procedure was discarded in favor of the equilibrium method.

RESULTS

The range of forces used was from 199 to 2698 grams, the maximum extension about 500 per cent. All runs were carried out with several strips of the same polymer, and were repeated from one to three times, except for GR-S-30 and NR-90, of which there was little available polymer. The values listed

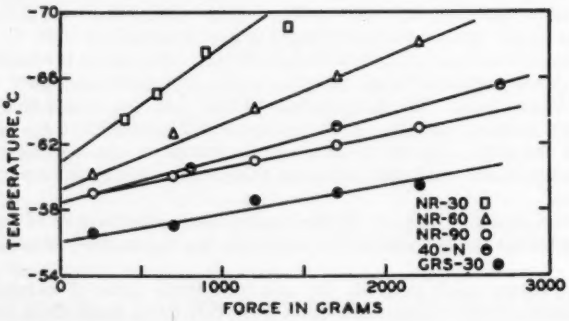


FIG. 1.

TABLE II

OBSERVED AND EXTRAPOLATED T_m IN ABSENCE OF FORCE

Polymer	T_m (extrapolated) (° C)	T_m (observed) (° C)	Slope (° C/g.)
NR-30	−61	−61	−0.0065
NR-60	−59	−58	−0.004
NR-90	−58.5	−63.5	−0.002
40-N	−58.5	−58.5	−0.003
GRS-30	56	−57	−0.002

in Table I are the averages calculated from all runs to the nearest one-half degree. The deviations from the mean were approximately ¾ of a degree.

It should be noted that the effect of 500 grams on T_m is of the order of the experimental error. Yet there is an unmistakable downward trend, sufficiently delineated that the slopes of the T_m vs. f curves can be measured. Surprisingly enough, despite the inexactness, plots of T_m vs. f give fairly good straight lines. Figure 1 shows the T_m vs. f curves for NR-30, NR-60, NR-90, 40-N, and GRS-30.

In Table II, the extrapolated values of T_m at zero force (determined from Figure 1) are given, together with those found directly by dilatometric means. Also included are the slopes of T_m vs. f curves.

The agreement between the temperature obtained in the two ways is quite good except for NR-90, supporting the view that the application of force does not result in a new phenomenon. It is felt that the dilatometric measurement for NR-90 is a fault since the others in the series are in good agreement. Unfortunately it was not possible to repeat the experiment on NR-90, since no more of the polymer was available.

DISCUSSION

It is now widely accepted that second-order transitions in polymers are thermodynamic in nature, and are due to the onset of rotations of polymer chain segments. There has been some question about the reality of the transitions in the thermodynamic sense[4], and it was proposed by Spencer and Boyer[5] that the apparent transitions were strictly a rate effect and due perhaps to viscous flow. However, Nolle[6] pointed out that Spencer and Boyer's argument is inconsistent with elasticity measurements, and Buchdahl and Neilsen[7], agreeing that part of the effect is rate inspired, asserted that a thermodynamic transition truly exists. They considered what types of internal phenomena would result in a transition, rejected on various grounds all but hindered rotation, and concluded that the transition is due to the onset of rotations.

The above point of view is taken here, since it is believed that the assumption of rotation, together with a knowledge of the internal structure of a polymer and the effects of external conditions on that structure, are sufficient to explain qualitatively the second-order transition phenomena. This approach is, or course, not new, and we have only extended it to cover the effect of force on rubber of different amounts of cross-linking.

Rotations.—A rubberlike material is assumed to consist of long polymer chains, with a structure roughly as follows. The individual chains are more or less coiled up on themselves, they are connected to one another or to themselves by cross-linking at various points along the chains, and they are also intertwined (without actual connecting points).

At temperatures above absolute zero, the chains are in continuous motion, and these motions are complex, for example, combinations of bending and twisting. As the temperature is raised, these motions become more violent, causing the chains to move farther apart, subject, however, to the constraint of cross-linking.

Now suppose we have started at a low temperature. When the temperature is raised high enough, the chains will have moved sufficiently far apart or uncoiled enough so that segments of the chains, or perhaps groups attached to the chains, will now be able to rotate about their bonds without interference from portions of their own chain or nearby chains. It is at this point that we assume the second-order transition appears.

Of course, not every chain will be separated by just the right distance at exactly the same temperature, because of local looseness or occasional crowding and excessive entanglements. Hence a few chains will commence rotation at a slightly lower temperature than the others, and a few will still be too entangled after the great majority are already rotating; thus the T curve should be somewhat rounded in the region of the transition, which is actually observed. It is to be expected however, that the bulk of the chains will begin rotation over a small temperature range, since the rotation of a few chains will make easier the rotation of neighboring chains.

The hypothesis that second-order transitions are caused by the onset of rotations seems to have first been put forth by Alfrey and Mark[8] and by Tuckett[9], who used it to explain the differences in T_m for different polymers. It would certainly be expected, for example, that there would be a definite change in the heat capacity, since the new type of motion would require extra energy.

Effect of tension.—Suppose a force of extension is applied to an unstrained polymer strip. Since extension increases the end-to-end separations, the chains tend to straighten out, not only by uncoiling, but also by disengaging themselves from their neighbors. Hence the chains, or substantial portions thereof, will, on the average, suffer less interference with their motion than when they are unstrained. Owing to this less kinked condition, rotation can now occur when the chains are closer to each other. But since the chains of the extended polymer need not be so far apart to begin rotation, their thermal motions will bring them to the required separation at a lower temperature than that needed for an unstrained strip. A larger applied force would accentuate this unkinking, and would permit the onset of rotations at an even lower temperature. The lowering of the transition temperature with applied force is, thus, a simple and natural consequence of the proposition that chains can rotate more easily when straightened out.

This is clearly verified for rubber and GR-S by the results of this research, as seen from Figure 1 and Table I. The extent of the effect depends on the polymer. Similar results have also been observed for Saran, polyvinyl chloride, and polystyrene[10].

We can also predict that the effect of force on T_m will become less at larger forces, i.e., T_m vs. f curves will level off. This behavior should be observed because, after the polymer strip is extended sufficiently, certain of the chains will be stretched out as far as they will go. Further extension of the polymer as a whole cannot increase the contribution toward easier rotation of these particular chains. The greater the extension, the greater will be the proportion of chains stretched to their maximum lengths, and the less will be the effect of added force on T_m. In fact, at that force where all the chains have been extended, T_m should not be affected at all by the application of additional force.

Owing to limitations of the size of the apparatus, it was not possible to use applied forces large enough to provide a clear proof for rubber and GR-S, although the results for NR-30 could be interpreted as just beginning to show the predicted behavior. The data for other polymers[10], however, do support this view.

Analogous arguments can be used to treat compression. Compression results in forcing the whole polymer structure closer together, so that a higher temperature will now be required to separate the chains by the distance necessary for rotation to begin. This prediction may be used to explain the data of Scott on rubber[11].

Effects of cross-linking.—We shall now consider polymers of the same stock, differing only in the extent of cross-linking. Increased cross-linking decreases the extent of possible rotation, because the greater number of binding points increases the amount of entanglement. Owing to this increased entanglement and the consequent restrictions on rotation, a more cross-linked polymer must be heated to a higher temperature than a less cross-linked one before the chains will be far enough apart to commence rotating.

This argument was presented some time ago by Tuckett[8] and Überreiter[12], and later by Nolle[6] and Buchdahl and Neilsen[7]. The predicted behavior has been verified for unstrained rubber by Tuckett[9] and Überreiter[12].

This effect has now also been observed for rubber and GR-S under tension, as inspection of Figure 1 shows. At any given force whatsoever, the values of T_m for the NR series are seen to increase in the order NR-30, NR-60, NR-90. But these are in the order of increased cross-linking, as expected.

We can also predict that, as the amount of cross-linking increases, the actual lowering of T_m by a given force decreases. This is true because increasing the number of cross-links increases the modulus, so a given force cannot extend the chains as far. Cross-linking thus inhibits the straightening out of the chains, which we saw makes rotation easier, and which causes T_m to occur at a lower temperature. In other words, the slopes of T_m vs. force curves should be flatter for polymers with a greater degree of cross-linking. Experimental verification of this proposition is found in the results of Table I and in Figure 1 for the NR series.

Effect of swelling agents.—While the phenomena discussed below are not directly related to our experiments except for one isolated measurement, they have been included to complete the discussion of factors affecting T_m.

Tuckett[9] has suggested that swelling agents and plasticizers should reduce hindrance to rotation, and thus decrease the value of T_m. Eley[13] has objected to this argument on the grounds that it is hard to see just why low molecular-weight compounds would reduce steric hindrance. It would appear that the reduction of steric hindrance is due to the swelling agent or plasticizer separating the chains, thus permitting them to rotate with less interchain interference. Eley's objection can be answered as follows. Small molecules move relatively independently of one another; a chain segment on the other hand is attached to others and its freedom of motion is thereby reduced. In other words, small molecules can be displaced much more readily by a chain segment than can one segment be displaced by another, whereby rotation is enhanced. The following analogy may be of service; it is easier to move a piece of seaweed through water than through a mass of other seaweed in water.

The predicted lowering of T_m has been observed many times with all sorts of plasticizers and compounds[14]. In this research, one sample of natural rubber was allowed to swell overnight in acetone at room temperature. The resulting

T_m was ten degrees lower than that of the unswollen sample. The observed[13] leveling of curves representing T_m vs. plasticizer added may be explained by noting that, after enough of the low-molecular plasticizer is added, most of the chains will be sufficiently separated by the plasticizer so that no further reduction in the hindrance to rotation can occur.

SYNOPSIS

The second-order transition temperatures of three different cures of natural rubber have been studied as functions of elongation by observing length dependence on temperature. This transition temperature (T_m) decreases with increasing applied force, and at any given force increases with increased cross-linking; moreover, the slopes of the T_m vs. force curves become less steep with increased cross-linking. The results are in agreement with the following propositions: (1) that transitions are caused by the onset of rotations; (2) that extension of the polymer makes the onset of such rotations easier, thus lowering T_m; (3) that increased cross-linking hinders rotation so as to increase T_m; and (4) that increased cross-linking diminishes the effect of a given force on T_m. The hypothesis of rotation is also discussed in connection with the effect of swelling agents on the second-order transition.

REFERENCES

[1] Boyer and Spencer, in Advances in Colloid Science, Interscience Publishers, New York, Vol. 2, p. 1.
[2] Müller, *Kolloid-Z.* **95**, 138 (1941).
[3] The polymers were obtained from the University of Akron through the courtesy of W. K. Taft.
[4] Alfrey, Goldfinger, and Mark, *J. Applied Physics* **14**, 700 (1943).
[5] Spencer and Boyer, *J. Applied Physics* **17**, 398 (1946).
[6] Nolle, *J. Polymer Sci.* **5**, 1 (1950).
[7] Buchdahl and Neilsen, *J. Applied Physics* **21**, 482 (1950).
[8] Alfrey and Mark, RUBBER CHEM. & TECHNOL. **14**, 525 (1941).
[9] Tuckett, *Trans. Faraday Soc.* **38**, 310 (1942). See also the discussion following the paper (*Trans. Faraday Soc.* **38**, 317 (1942).
[10] Müller, *Kolloid-Z.* **95**, 38 (1941); Boyer and Spencer, *J. Applied Physics* **10**, 594 (1945). Neither Müller nor Boyer and Spencer discussed their results in connection with rotations alone. Boyer and Spencer treated their results using the concept of viscous flow.
[11] Scott, *J. Research Natl. Bur. Standards* **14**, 99 (1935).
[12] Überreiter, *Kolloid-Z.* **102**, 272 (1943).
[13] Eley, *Trans. Faraday Soc.* **38**, 299 (1942).
[14] Boyer and Spencer, *J. Polymer Sci.* **2**, 157 (1947). See Table 1 in this paper for an extensive list of references on the effect of plasticizers.

VULCANIZATION STRUCTURES AND THEIR INFLUENCE ON THE HEAT RESISTANCE AND FATIGUE OF RUBBER *

B. A. Dogadkin and Z. N. Tarasova

Scientific Research Institute of the Tire Industry, Moscow, USSR

According to theories developed by the authors, vulcanized rubber is a system in which the molecular chains are united by local molecular and chemical bonds of varying intensity. The composition, concentration, distribution, and energy of these bonds determine the principal physical and mechanical properties of vulcanizates. For this reason the study of the structure of a vulcanizate is of primary practical importance. However, until recently there have been no reliable data in the scientific literature concerning the nature of vulcanization structures and methods of studying them. The question of the change of vulcanization structures during aging and fatigue and their effect on the intensity of these processes have not been treated at all. The present work is the second article based on studies made by the authors in this field.

THERMOMECHANICAL METHOD OF STUDYING VULCANIZED STRUCTURES

Any explanation of the nature of the bonds in a vulcanizate based on chemical methods is confronted with great obstacles, principally because it is impossible to analyze the individual chemical groups which compose the separate molecular chains and the bonds between the chains which are responsible for the development of spatial formations. From this point of view, the thermodynamic method worked out by the authors, which is based on the study of the relaxation of stress in vulcanizates in an inert gaseous atmosphere at various temperatures, is of unquestionable interest. This method is based on the following considerations.

As Dogadkin and Reznikovskiĭ have shown[1], the slow relaxation of stress in a vulcanizate at temperatures up to 70° C is caused by rupture of local intermolecular bonds and regrouping of the structural elements of the polymer chains, without destruction of the chemical bonds between them. For this reason, after some time at these temperatures, a practically equilibrium value of the modulus is established, which depends on the number of chemical bridge bonds, according to the equation:

$$E_\infty = 3\,N \cdot k \cdot T$$

where N represents the number of segments of the spatial network of the vulcanizate in a unit volume. Bartenev has suggested the more accurate equation:

$$\sigma_\infty = k \cdot N^{\frac{1}{3}} \cdot \xi$$

* Translated for Rubber Chemistry and Technology from the *Kolloidnyĭ Zhurnal*, Vol. 15, No. 5, pages 347–60 (1953).

At temperatures above 70° C, thermal decomposition of the stressed chemical bonds between the chains takes place, at a rate inversely proportional to the energy of activation of the decomposition process of the given type of bond. Studying the kinetics of stress relaxation at various temperatures under conditions which exclude oxidation processes, it is possible to develop a theory of the type of bonds which are decomposed in the spatial structure of the vulcanizate. In particular, in the case of sulfur vulcanizates, it is possible to assume the existence of the following types of bonds between the rubber chains: (1) —C—C—, formed as a result of polymerization processes; (2) —C—S—C— monosulfides; (3) —C—S—S—C— disulfides; and (4) —C— —S_x—C— polysulfides, formed as a result of the direct participation of the vulcanizing agent, sulfur, in the process of union of the molecular chains.

The energy of the —C—C— bonds, determined approximately, is 62.7 kcal. per mole; that of the —C—S— bonds 54.5 kcal. per mole. The energy of the S—S— bonds is determined in various ways, depending on the type of radicals bound with the sulfur atoms. According to data of Eyring, it is 27.5 kcal. per mole for polysulfide compounds.

Naturally the heat resistance of a vulcanizate will depend on which of the types of bonds indicated is predominant. In order to measure the heat resistance of a vulcanized structure, the authors and M. M. Reznikovskiĭ devised a new type of dynamometer which makes possible the study of the relaxation of stress of the specimens in an inert gaseous atmosphere (nitrogen) in a wide range of temperatures. The slightest amount of oxygen can cause a distortion of the results, since, in this case, a heat oxidation process and not a thermal process of decomposition of the structure of the vulcanizate takes place.

The dynamometer is constructed by using as deforming mechanism a float, whose weight and deformation are determined by the depth of immersion in mercury, which in turn is regulated by a siphon.

Figure 1 shows schematically the floating dynamometer. The dynamometer consists of a thick-walled cylinder of molybdenum glass 1, the upper part of which (the operating chamber) is surrounded by a jacket heated by a hot liquid pumped from an ultrathermostat. The cylinder is covered by a ground-glass cover 2, with an opening for a thermometer, and ends in an outlet which is connected with flask 4 by a flexible rubber tube. The lower part of the cylinder, (the float chamber) is filled with mercury, the level of which is determined by the position of flask 4, which can be moved up and down by means of a running screw 5.

The specimen to be studied, in the form of a strip, is fastened in a stationary clamp and in a movable clamp. The stationary clamp is fixed to the top of the dynamometer float 9. The length of the deformed strip can be determined according to the position of the float on the scale. From measurements of the depth of immersion of the float, it is possible to calculate the force which deforms the specimen. The stopcock 11 makes it possible to connect the apparatus with a vacuum, and then with the source of nitrogen.

After the specimen is stretched to a given deformation, the deformation begins to increase further as the result of the fall of stress; this takes place when the float spontaneously descends. When measurements are made at definite intervals, by moving the handle 12, the dynamometer float rises back to a position corresponding to a given deformation of the specimen.

A graph $\sigma/\sigma_0 = f(t)$ for the fall of stress with time can be constructed from experimental data obtained. The experiments showed that, within the range up to $\xi \approx 100$ per cent, the course of the curves does not depend on the initial

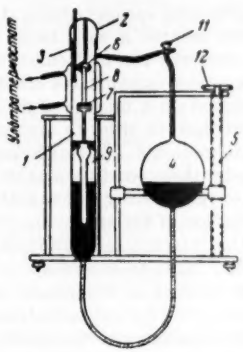


FIG. 1.—Diagram of the float dynamometer.

1. Molybdenum glass cylinder.
2. Cover.
3. Thermometer.
4. Flask
5. Running screw.
6. Upper clamp.
7. Lower clamp for the test-specimen.
8, 9. Float with scale.
10. Tube.
11. Three-way stopcock.
12. Head of running screw.

value of the deformation (Figure 2). In the experiment where the process takes place at temperatures below 70° C, it follows the laws established for relaxation phenomena involved in regrouping of the molecular chains, without destruction of the chemical bonds[1]. At higher temperatures, as has already been observed, decomposition of the chemical bonds of the vulcanized structure takes place, and the phenomenon follows laws discussed later in this article. The kinetic constant from the equation describing stress relaxation at temperatures above 100° C can be applied to the comparative characteristic of heat resistance.

OBJECTS OF INVESTIGATION

Unloaded vulcanizates of natural rubber and butadiene-styrene (SKS-30) copolymers of three types were chosen for study: (1) with sulfur alone without accelerator; (2) without sulfur, but with tetramethylthiuram disulfide as vul-

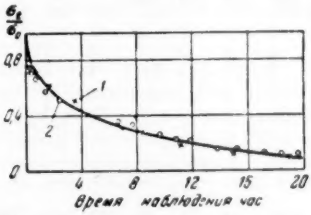


FIG. 2.—Relation between the relative rate of relaxation and the deformation.

Circles—100 per cent.
Crosses— 60 per cent.

The abscissa represents the *Time in hours*,

canizing agent; (3) with sulfur and various accelerators. These different compositions of the vulcanizates assured a wide range of contents of the abovementioned types of bonds between the molecular chains of the rubber. The composition and properties of the vulcanizates are listed in Table 1.

The mixtures were prepared on a micro-roll mill, placed in a hermetically sealed cabinet filled with nitrogen in order to prevent absorption of oxygen at the moment of mixing the ingredients. It was found that preparation of mixtures of unmilled rubber under these conditions is an indispensable condition in excluding the influence of oxygen during vulcanization and during the subsequent experiments. Evacuation of the specimens with a mercury pump, used by many investigators for this purpose, is insufficient, does not assure "oxygen-free" experiments, and often leads to erroneous conclusions. The mixtures were placed in the nitrogen cabinet in cellophane packages, which were then placed between the plates of a press for vulcanization. Vulcanization was continued to a state roughly corresponding to the optimum physical and mechanical properties, at which point the vulcanizates possessed practically the same values of the equilibrium modulus and maximum degree of swelling. In particular, all the vulcanizates of natural rubber had a concentration of chemical bonds between the chains equal to $7–8 \times 10^{19}$ cc.$^{-1}$. and the vulcanizates of the butadiene-styrene copolymers had a concentration equal to $10–11.5 \times 10^{19}$ cc.$^{-1}$. The number of cross-links was calculated by the equation of Flory[2].

DETERMINATION OF POLYSULFIDE SULFUR

It is known that the labile sulfur of organic polysulfides can be removed by boiling with a solution of sodium sulfite[3], which converts the latter into thiosulfate. This reaction was used by the authors for determining the polysulfide contents of the vulcanizates. The degree of extraction depends on the concentration of the sodium sulfite solution and the time of heating. Sufficiently reproducible results are obtained with the following procedure. The vulcanizates are extracted for 50 hours with cold acetone to eliminate free sulfur. After this, a batch of finely divided vulcanizate is heated in a 10 per cent boiling solution of sodium sulfite for 50–70 hours, with five changes of liquid (until no more thiosulfate is detected in the last extract). The extracts are combined,

TABLE 1

COMPOSITION OF VULCANIZATES AND THEIR PROPERTIES

Ingredient											
Smoked-sheet rubber	100	100	100	100	—	—	—	—	—	—	—
SKS-30 synthetic rubber	—	—	—	—	100	100	100	100	100	100	100
Sulfur	7	—	7	3	7	—	7	3	2	1.7	3
Zinc oxide	5	5	5	5	5	5	5	5	5	5	5
Stearic acid	1	1	1	1	1	1	1	1	1	1	1
Tetramethylthiuram disulfide	—	3	—	—	—	3	—	—	—	—	—
Diphenylguanidine	—	—	1	—	—	—	1	—	0.75	—	—
Mercaptobenzothiazole	—	—	—	1	—	—	—	1	—	—	—
Benzothiazolyl disulfide	—	—	—	—	—	—	—	—	0.6	—	2
Vulkacit	—	—	—	—	—	—	—	—	—	1.2	—
Optimum time in minutes	240	60	35	15	160	65	30	35	25	40	40
Tensile strength (kg. per sq. cm.)	275	286	350	265	50	45	59	22	—	—	—
Relative elongation (%)	700	760	800	850	680	320	565	480	—	—	—
Swelling maximum (%)	432	440	410	—	362	316	373	340	290	320	355

TABLE 2

CONTENT OF BOUND SULFUR ELIMINATED WITH SODIUM SULFITE

Type of vulcanizate	Vulcanizing system	Total bound sulfur (%)	Bound sulfur eliminated by sodium sulfite (%)	Proportion of sulfur eliminated by sodium sulfite
HK-1	7% sulfur without accelerator	5.2	0.245	4.7
HK-2	3% Thiuram without sulfur	0.7	0	0
HK-3	7% sulfur + 1% diphenylguanidine	4.7	0.820	16.8
HK-4	3% sulfur + 1% mercaptobenzothiazole	2.8	0.108	3.8
SK-1	7% sulfur without accelerator	1.7	0.835	48.8
SK-3	7% sulfur + 1% diphenylguanidine	1.6	0.256	16.3
SK-4	3% sulfur + 1% mercaptobenzothiazole	2.8	0.081	2.8

and the thiosulfate is titrated back with iodine solution. The results of these measurements are shown in Table 2.

As is seen from Table 2, the vulcanizates differ notably with respect to the amount of "polysulfide" sulfur extracted. The vulcanizate prepared without accelerator and the vulcanizate containing 7 per cent sulfur and 1 per cent diphenylguanidine contain the largest percentage of this type of sulfur. The vulcanizate prepared by heating with thiuram contains no sulfur at all extractable by sodium sulfite solution. As will be explained in detail in the latter part of this work, these results agree well with the vulcanization mechanism assumed, and are proof that the reaction with sodium sulfite can actually serve to determine the sulfur content of groups of the type $R_1—S_n—R_2$. However, this result must be regarded as only approximate, inasmuch as the course of the sodium sulfite reactions depends on the number of sulfur atoms composing the polysulfide, their distribution, and the nature of R_1 and R_2 radicals.

DETERMINATION OF BOUND SULFUR CONTENT IN THE FORM OF ZINC SULFIDE

Determination of the amount of zinc sulfide in specimens of vulcanizates extracted with acetone was used by the authors as an indirect method of determining the presence of disulfide bridges $R_1—S—S—R_2$. According to contemporary theories, developed by a number of authors[4], the reaction of rubber with sulfur in the presence of soluble zinc compounds takes place according to the following reaction:

$$RH \xrightarrow{S} RS \xrightarrow{Zn} RSZnSR \xrightarrow{S} RSSR + ZnS$$

where R is the rubber hydrocarbon.

In the extensive study of Hall, Olsen and others[5], the above process was experimentally proved for the formation of zinc sulfide when biphenylthiol is heated at 143° with sulfur in the presence of zinc salts of fatty acids and mercaptobenzothiazole, and during the reaction of simple olefins with sulfur in the presence of zinc salts and mercaptobenzothiazole. According to these studies, the zinc sulfide content of a vulcanizate is equivalent to the content of disulfide bonds of $R_1—SS—R_2$ type.

Zinc sulfide was determined by the authors in samples of vulcanizates extracted with acetone for 50 hours. In the presence of hydrochloric acid, the zinc sulfide is decomposed, with the formation of hydrogen sulfide, which is

TABLE 3

ZINC SULFIDE CONTENT IN VULCANIZATES OF NATURAL RUBBER

Type of vulcanizate	Vulcanizing system	Total bound sulfur in form of zinc sulfide (%)	Proportion of bound sulfur in form of zinc sulfide (%)	Content of disulfide equivalent to zinc sulfide (%)
HK-1	7% Sulfur without accelerator	5.19	0.57	22.4
HK-2	3% Thiuram without sulfur	0.70	0.02	4.8
HK-3	7% Sulfur + 1% diphenylguanidine	3.41	0.62	36.4
HK-4	3% Sulfur + 1% mercaptobenzothiazole	2.79	0.22	15.4

removed by a current of nitrogen and caught in absorption vessels by cadmium acetate, and then is titrated back with potassium iodide in an acid medium.

Table 3 gives data from measurements of the zinc sulfide contents of vulcanizates of natural rubber.

RELAXATION OF STRESS IN VULCANIZATES OF NATURAL AND BUTADIENE-STYRENE RUBBER

Figure 3 gives the relaxation of stress in vulcanizates of natural rubber with various accelerators at 70° and 100° C for 100 per cent deformation in a nitrogen atmosphere. At 70° C (Curve 1), a decrease of stress takes place in all the vulcanizates at a uniform rate up to 90 per cent of the original value, and then remains practically constant. The residual deformation was measured after the specimens had been swollen in benzene vapor and the solvent had then been removed in order to secure more favorable relaxation conditions.

At 100° C, a difference appears in the behavior of the vulcanizates. In rubbers containing no accelerator and those prepared by heating with 7 per cent sulfur and 1 per cent diphenylguanidine, an almost total drop in stress is observed, while the residual deformation is ~80 per cent of the original value. Vulcanizates with tetramethylthiuram disulfide are relaxed, at 100° C in 20 hours, to 70 per cent of the original stress, after which the stress remains practically constant. The residual deformation is not more than 20 per cent.

The great heat resistance of the bridges of vulcanizates with thiuram and also with mercaptobenzothiazole is evident at 130° C (Figure 4). In this case, the stress falls in 65 hours to 5 per cent of its original value, while the time re-

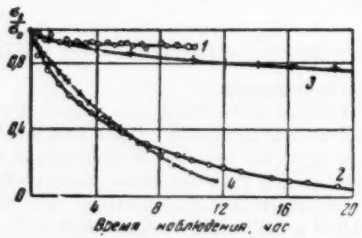


FIG. 3.—Relaxation of stress in natural rubber vulcanizates during heating in nitrogen

1. For all vulcanizates at 70° C.
2. For a vulcanizate containing diphenylguanidine.
3. For vulcanizate containing Thiuram.
4. Without accelerator at 100° C.

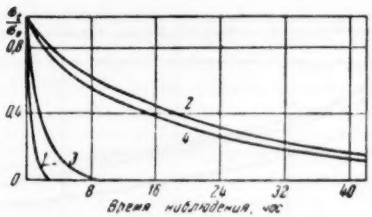


FIG. 4.—Relaxation of stress in natural rubber vulcanizates in a nitrogen atmosphere at 130° C.

1. Without accelerator.
2. With diphenylguanidine.
3. With tetramethylthiuram disulfide.
4. With mercaptobenzothiazole.

The abscissa represents the *Time in hours.*

quired for total loss of stress for vulcanizates with diphenylguanidine is 8 hours, and for vulcanizates without accelerator, 4 hours. In the latter case, the deformation is permanent; in other words, extensive decomposition of the chemical bonds of these vulcanizates is manifest.

The experiments of stress relaxation in vulcanizates of butadiene-styrene rubber were made under the same conditions as for natural rubber, but with a deformation of 60 per cent. This deformation was chosen because, in the case of vulcanizates with thiuram, the specimen is destroyed at 100 per cent elongation before the relaxation process is finished.

At 70° C (Figure 5) the stress in all types of vulcanizates falls to a definite value, viz., 60–80% of the original value. This final stress remains unchanged during 80–90 hours. At 100° C (Figure 6) the stress in vulcanizates without accelerator, in vulcanizates with diphenylguanidine, and in vulcanizates with mercaptobenzothiazole, falls to 15 per cent of its original value in 40, 52, and 70 hours, respectively. In the vulcanizate with thiuram, the stress falls in 50 hours to 90 per cent of its original value, and then remains at this level. At 130° C (Figure 7), vulcanizates with thiuram without sulfur are also characterized by their great heat resistance; in 50 hours the stress falls to 60 per cent of the original value and then remains constant for 20 hours, while the stress in sulfur vulcanizates with other accelerators falls at a much faster rate, viz., 5–20 per cent of the original value.

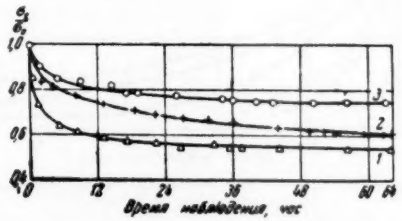


FIG. 5.—Relaxation of stress in vulcanizates of butadiene-styrene rubber in a nitrogen atmosphere at 70° C.

1. Without accelerator.
2. With diphenylguanidine.
3. With mercaptobenzothiazole.

The abscissa represents the *Time in hours.*

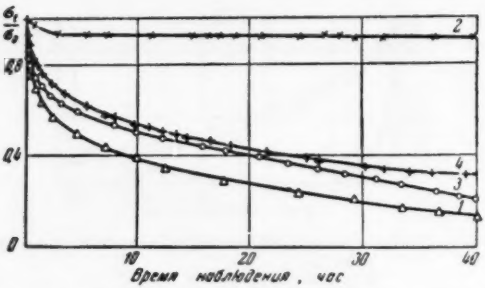


FIG. 6.—Relaxation of stress in vulcanizates of butadiene-styrene rubber in a nitrogen atmosphere at 100° C.

1. Without accelerator.
2. With Thiuram.
3. With diphenylguanidine.
4. With mercaptobenzothiazole.

The abscissa represents the *Time in hours.*

Comparing the data for stress relaxation of vulcanizates of SKS-40 with corresponding experiments for natural rubber, we are led to the conclusion that the general character of the process is the same, but that the rate of relaxation of all SKS-30 vulcanizates, with the exception of those containing mercaptobenzothiazole, is much lower (see Table 5).

An essential difference of SKS-40 vulcanizates is also that the permanent part of their deformation is much less than that of vulcanizates of natural rubber.

CHANGE OF SWELLING LIMIT DURING RELAXATION

It is known that the swelling maximum of a vulcanizate in hydrocarbon solvents depends on the number of bridges in the vulcanized structure[2]. As has been mentioned, we studied vulcanizates containing approximately the

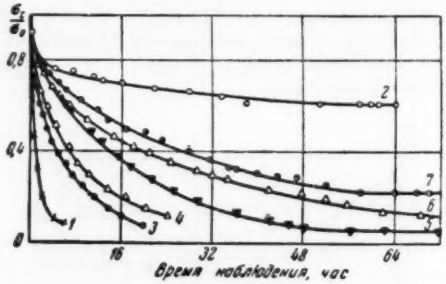


FIG. 7.—Relaxation of stress in vulcanizates of butadiene-styrene rubber in a nitrogen atmosphere at 130° C.

1. Without accelerator.
2. With Thiuram.
3. With diphenylguanidine.
4. With mercaptobenzothiazole.
5. With diphenylguanidine + benzothiazolyl disulfide.
6. With Vulkacit-A cet.
7. With benzothiazolyl disulfide.

The abscissa represents the *Time in hours.*

same concentration of chemical bonds between the chains, which, according to the swelling data, is 7–8 × 10^{19} cc.$^{-1}$ for natural rubber and 10–12 × 10^{19} cc.$^{-1}$ for SKS-30. The decomposition of vulcanized structures and the resulting change of the number of bridges in the vulcanizate naturally must be accompanied by a change of the swelling maximum. In Table 4, data on the swelling of the specimens studied, before and after relaxation, are shown. In every case, after heating of strained natural-rubber vulcanizates, a large increase of the swelling maximum (up to 70 per cent of the original size) is observed. This indicates a sharp decrease of the number of cross-links in the structure of the vulcanizate. On the other hand, vulcanizates of butadiene-styrene rubber show decreases although small, of the swelling maximum; in other words, heating of these vulcanizates is accompanied by an increase, not a decrease, of the number of bridge bonds. It may be presumed that this increase is due to

TABLE 4

CHANGE OF PROPERTIES OF VULCANIZATES AS A RESULT OF RELAXATION OF STRESS AT 130° C

Type of vulcanizate	Type of accelerator	Swelling maximum in %		Relative swelling maximum $\Delta Q/Q$	Permanent deformation in %	Bound sulfur content in %	
		In original specimens	After relaxation			In original specimens	After relaxation
HK-1	Sulfur without accelerator	433	565	+0.30	100	—	—
HK-2	Thiuram without sulfur	477	765	+0.70	43	—	—
HK-3	Diphenylguanidine	410	603	+0.46	100	—	—
SK-1	Sulfur without accelerator	362	349	−0.03	57	1.7	3.2
SK-2	Thiuram without sulfur	316	348	+0.10	26	—	—
SK-3	Diphenylguanidine	346	306	−0.12	48	2.8	3.0
SK-4	Mercaptobenzothiazole	338	306	−0.09	51	2.0	3.7
SK-5	Diphenylguanidine	290	252	−0.14	46	—	—
SK-6	Vulkanacit-AZ	312	274	−0.13	60	—	—
SK-7	Diphenylguanidine	355	220	−0.40	48	—	—
SK-1	Without accelerator	362	479	+0.25	61	—	—
SK-3	Diphenylguanidine	373	438	+0.20	60	—	—

further combination of sulfur in the vulcanizate. In fact, experiments have shown that the bound-sulfur content increases during relaxation, but a vulcanizate extracted with acetone, and not containing free sulfur, shows an increase of the swelling maximum after heating.

RELAXATION MECHANISM AND INFLUENCE OF VULCANIZATION STRUCTURES ON THE HEAT RESISTANCE OF VULCANIZATES

As may be seen from Figure 3, the fall of stress at 70° C in all the vulcanizates of natural rubber studied proceeds at a uniform rate down to 90 per cent of the original value. In this case, the typical process of slow relaxation appears, owing to rupture of local intermolecular bonds and regrouping of the structural elements of the molecular chains. Inasmuch as the nature of the intermolecular reactions is, in general, the same for all vulcanizates, the decrease of stress in various vulcanizates at 70° C takes place at approximately the same rate.

In vulcanizates of natural rubber, the relaxation of stress at a temperature above 100° C, due to regrouping of the molecular chains, proceeds rapidly during the first minutes of observation. A further and large decrease of stress (to zero in some vulcanizates) is caused by destruction of the chemical bonds of the vulcanized structure.

It is natural to assume that the thermal decomposition of the chemical bonds subjected to stress follows a monomolecular law. Recombination of the free radicals thus formed takes place, with formation of cross-links which do not undergo stress, since the degree of deformation under the experimental conditions does not change. Proceeding from these assumptions and assuming that,

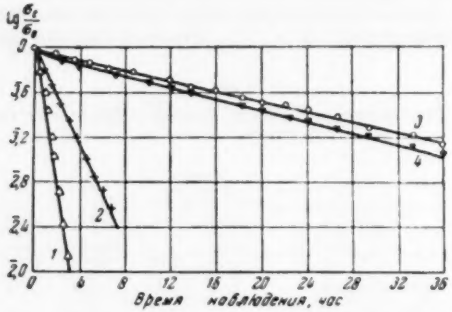


FIG. 8.—Relaxation of stress in natural-rubber vulcanizates at 180° C represented as coordinates.

1. For all vulcanizates at 70° C.
2. Vulcanizate with diphenylguanidine.
3. With Thiuram.
4. Without accelerator at 100° C.

The abscissa represents the *Time in hours.*

in accord with contemporary theories of elasticity, the stress σ is proportional to the number of cross-links n, we write:

$$-\frac{d\sigma}{dt} = k_1 \cdot \frac{dn}{dt} = k(n_0 - x)$$

where n_0 is the original number of chemical bonds between the chains and x is the number of bonds decomposed at the moment t. After integrating, we obtain:

$$\sigma_t = \sigma_0 \cdot e^{-kt}$$

where σ_0 is the initial equilibrium stress and σ_t is the stress at the moment t. In fact, as may be seen in Figures 8 and 9, at 130° C the value of $\ln \sigma_t/\sigma_0$ is a linear function of the relaxation time in a broad range of observations. The deviation from a linear relation observed with vulcanizates of butadiene-styrene rubber in the initial stage is explained by the fact that, in this period, the relaxation process is especially pronounced, owing to regrouping of the molecular non-valence bonds. In this case, σ_0 is found by extrapolating the linear part of the graph $\log \sigma = f(t)$.

From the equation: $\sigma_t = \sigma_0 \cdot e^{-kt}$, the values of the kinetic constant k, which characterize the rate of decomposition of the vulcanized structures, were calculated from the slope of the curves in Figures 8 and 9. These constants serve

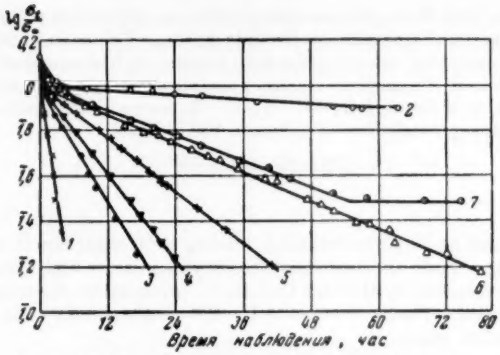


FIG. 9.—Relaxation of stress in vulcanizates of butadiene-styrene rubber at 130° C, represented as coordinates.

1. Without accelerator.
2. With Thiuram.
3. With diphenylguanidine.
4. With mercaptobenzothiazole.
5. With diphenylguanidine + benzothiazolyl disulfide.
6. With Vulkacit A-cet.
7. With benzothiazolyl disulfide.

The abscissa represents the *Time in hours*.

as a measure of the heat resistance of vulcanizates. In Table 5, the values of the kinetic constants are shown for 130° C.

As is evident from Table 5, the rate of thermal decomposition of vulcanized structures depends primarily on the type of vulcanizing group. A good correlation is observed between the heat resistance of a vulcanizate, determined from the kinetic constant of the relaxation process, and the contents of polysulfide and disulfide bonds, determined by chemical methods. Vulcanizates with Thiuram without sulfur have the greatest heat resistance ($k = 8.6 \times 10^{-4}$).

TABLE 5

KINETIC CONSTANTS OF THE RELAXATION PROCESS IN VULCANIZATES 130° C IN NITROGEN AND THE CONTENT OF POLYSULFIDE SULFUR

Type of vulcanizate	Vulcanizing system	Kinetic constant of relaxation process K (min.$^{-1}$)	Total bound sulfur content (%)	Proportion of bound sulfur eliminated by sodium sulfite (%)	Proportion of bound sulfur in form of zinc sulfide (%)
HK-1	7% sulfur without accelerator	2.4×10^{-3}	5.2	4.7	11.2
HK-2	3% Thiuram without sulfur	8.6×10^{-4}	0.7	0	2.4
HK-3	7% sulfur + 1% diphenylguanidine	8.5×10^{-3}	4.7	16.8	18.2
HK-4	3% sulfur + 1% mercaptobenzothiazole	1.0×10^{-3}	2.8	3.8	7.7
SK-1	7% sulfur	7.5×10^{-3}	1.7	48.8	—
SK-2	3% Thiuram	3.2×10^{-5}	0.7	—	—
SK-3	7% sulfur + 1% diphenylguanidine	1.4×10^{-3}	1.6	34.3	—
SK-4	3% sulufr + 1% mercaptobenzothiazole	1.3×10^{-4}	2.8	2.8	—
SK-5	2% sulfur + 0.75% diphenylguanidine 0.6% benzothiazolyl disulfide	$7.7\ 10^{-4}$	—	—	—
SK-6	1.7% sulfur + 1.2% Vulkacit	$3.9\ 10^{-4}$	—	—	—
SK-7	3% sulfur + 2% benozthiazolyl disulfide	$3.7\ 10^{-4}$	—	—	—

Analysis shows that these vulcanizates contain no polysulfide sulfur, and contain only a very small quantity of disulfide sulfur. This is in accord with the mechanism proposed for vulcanization with tetramethylthiuram disulfide. The latter, as is known, decomposes during vulcanization, releasing sulfur atoms, which are capable of forming $R_1—C—S—C—R_2$ monosulfide bonds. Furthermore in the disproportionation of thiuram, the radicals

$$(CH_3)_2N—C(=S)—S—S^*$$

are formed, which cause polymerization, leading to stronger bonds of the type[6], $R_1—C—C—R_2$. Thus, the heat resistance of vulcanizates with thiuram (without sulfur) is explained by the fact that their vulcanization structure contains chiefly the stronger —C—S—C— and —C—C— bonds and does not contain the weaker polysulfide bonds.

Vulcanizates prepared with sulfur and without accelerator have the largest constant of rate of thermal decomposition ($k = 2.4 \times 10^{-2}$). These same vulcanizates, according to data from chemical analysis, contain the largest contents of polysulfide and disulfide bonds (Table 5). The presence of polysulfide bonds in these vulcanizates is evidently explained by the fact that the initial step in vulcanization is the opening of the eight-member ring, S_8, characteristic of elemental sulfur, with the formation of the biradical:

$$S_8 \rightleftarrows —S—S—S—S—S—S—S—S—$$

This biradical either itself unites directly with the molecular chains of the rubber, or else breaks up into new radicals containing a variable number of sulfur atoms, S_n, which then unite the rubber molecules. In both cases, the vulcanized structure contains a large number of unstable polysulfide bonds.

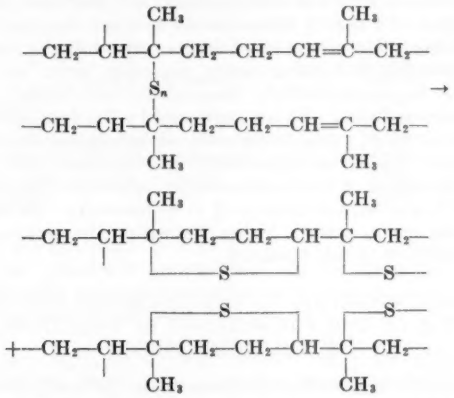
Vulcanization accelerators[7] facilitate this transformation of the elemental sulfur, which decreases the content of sulfur atoms in the bridge bonds. In this respect, accelerators behave differently. Some vulcanization accelerators, breaking down into free radicals, can induce polymerization processes, with the formation of —C—C— bonds in the vulcanization structure. Among such accelerators are benzothiazolyl disulfide and Vulkacit, which give heat-resistant stable vulcanizates ($k = 3.9 \times 10^{-4}$). The proportion of sulfur to accelerator undoubltedly influences the nature of the vulcanization structures.

The type of rubber is of essential importance the nature of the bonds in a vulcanizate; in particular, vulcanizates of butadiene-styrene rubber possess greater heat resistance than natural rubber vulcanizates, owing to the presence in the former of a relatively large proportion of —C—C— bonds, which are formed as a result of polymerization processes. The existence of these processes was established by Dogadkin, Bartenev, and Novikov[8] from a study of the kinetic curves of the change of modulus during vulcanization of butadiene-styrene rubber.

A proof of the presence of strong chemical bonds in vulcanizates of butadiene-styrene rubber is the fact that, in distinction from natural rubber, the decrease of stress at 130° C does not continue to zero, but reaches a constant value, which differs for different types of accelerators.

As a result of the decomposition of intermolecular bonds in all vulcanizates of natural rubber, the swelling maximum in xylene is greatly increased (Table 4); this attests to a decrease of the number of cross-links between the molecular chains of the rubber, regardless of further absorption of sulfur.

This fact is of great interest, and can be explained by the assumption that recombination of free radicals which are formed during the decomposition of vulcanization structures is accompanied by closing of the intramolecular ring. This process can be represented schematically as follows:



Relaxation of stress in vulcanizates of butadiene-styrene rubber at 130° C is accompanied by a slight decrease of the swelling maximum. However, if a vulcanizate, extracted for 50 hours with acetone to eliminate free sulfur, is heated, the stress relaxation leads to an increase of the swelling maximum (compare the specimens of SK-1 and SK-3 with the specimens of SK-1e and SK-3e in Table 4). Thus, the increase of density of the network of a vulcanizate after relaxation in unextracted specimens must be ascribed to conversion of a part of the free sulfur to the bound state (post-vulcanization), confirmed by the data of direct analysis presented in Table 4.

The formation of cyclic intramolecular formations in butadiene-styrene rubber is hindered by the presence of side vinyl and phenyl groups. Hence,

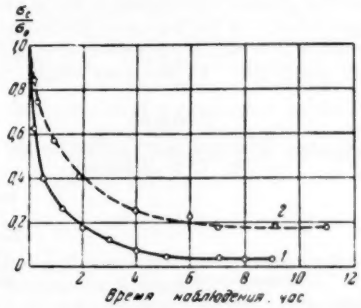


FIG. 10.—Two relaxation cycles in a butadiene-styrene rubber vulcanizates with diphenylguanidine as accelerator at 130° C in nitrogen.

1. First relaxation cycle.
2. Second relaxation cycle.

The abscissa represents the *Time in hours*.

recombination of the radicals which are formed during the thermal decomposition of the vulcanization structure of a rubber evidently is often accompanied by the formation of new cross-links in the unstressed segments of the vulcanization network. In the general case, the decomposition of each cross-linkage leads to the formation of two or more radicals, and therefore, after recombination, the formation of a denser vulcanization network than in the original vulcanizate is possible. The new cross-linkages formed during recombination of the radicals possess higher bonding energy, since the "order" of union decreases —the polysulfide bonds are partially transformed into disulfide bonds, and the disulfides into monosulfides. This is confirmed by the data of Figure 10, where two relaxation curves of vulcanizates with diphenylguanidine are shown; the first curve refers to the original specimen (first relaxation cycle) and the second describes the relaxation of the same specimen after the first relaxation cycle, again stretched to the same elongation (ξ = 60 per cent). As is seen, the curve of the second relaxation cycle is higher, indicating the presence of a stronger vulcanization network in this specimen.

THERMAL DECOMPOSITION OF VULCANIZATION STRUCTURES AS A FACTOR OF THE PHENOMENON OF VULCANIZATION OPTIMUM (REVERSION)

According to theories developed by one of the authors[9], the phenomenon of vulcanization optimum (reversion) is connected with the simultaneous processes of structure formation and destruction of the rubber hydrocarbon during vulcanization. In a number of previous studies we investigated the structural processes which are caused by the reaction of the vulcanizing agent with oxygen. The data presented in the present work indicate the possibility of purely thermal processes of destruction of vulcanization structures. In Table 6, data are shown for the change of swelling maximum as a result of heating vulcanizates of butadiene-styrene rubber at 130° C in the absence of oxygen in the unstressed and stressed states. In the first case an increase, in the second case, a decrease of the swelling maximum is observed. Thus, it has been proved experimentally that at 130° C (lower than the usual vulcanization temperatures) a decomposition of vulcanization structures also takes place in the unstressed state. The ultimate result of this process with respect to the physical-chemical properties of the vulcanizate depends on the nature of the secondary processes which cause a stabilization of the free radicals formed during the thermal decomposition of vulcanization structures. In the case where recombination of the

TABLE 6

CHANGE OF SWELLING MAXIMUM DURING HEATING OF VULCANIZATES AT 130° C IN NITROGEN

Type of vulcanizate	Vulcanizing system	Swelling maximum in %		
		Original vulcanizate	After heating	After vulcanization
SK-2	3% Thiuram	316	349	348
SK-3	4% sulfur + 1% diphenylguanidine	286	312	263
SK-4	3% sulfur + 1% mercaptobenzothiazole	338	340	306
SK-5	2% sulfur + 0.7% sulfur + 1.2% Vulkacit	290	408	252
SK-6	1.7% sulfur + 1.2% Vulkacit	283	320	165*

* After two relaxation cycles.

TABLE 7

TENSILE STRENGTH OF SKS-30 VULCANIZATES UNDER CONSTANT LOAD AT 100° C IN NITROGEN

Type of vulcanization	Vulcanizing system	Tensile strength in cycles	Change of swelling maximum in %	
			Original vulcanizate	After fatigue
SK-1	7% sulfur	7,200	—	—
SK-2	3% Thiuram	10,800	284	306
SK-3	7% sulfur + 1% diphenylguanidine	12,000	298	332
SK-4	3% sulfur + 1% mercaptobenzothiazole	44,600	—	—
SK-6	1.7% sulfur + 1.2% Vulkacit	27,300	—	—
SK-7	3% sulfur	33,100	—	—

radicals leads to the formation of a predominantly intramolecular ring or the stabilization of the radicals is accomplished by the formation of functional groups not entering into the spatial structure of the vulcanizate, such a process leads to the phenomenon of vulcanization reversion.

EFFECT OF VULCANIZATION STRUCTURE ON THE RESISTANCE OF RUBBER TO REPEATED DEFORMATIONS (FATIGUE)

The nature of vulcanization structures is of the utmost importance in determining the resistance of vulcanizates to repeated deformations or to destruction. However, this question has hitherto not been discussed in the scientific literature. The particular vulcanizates of butadiene-styrene rubber studied by the authors were subjected to repeated deformations in a specially constructed apparatus, in which cyclic deformations of the specimens (240 cycles per minute) were effected at approximately constant load by moving a load with a magnetic mechanism. The specimens were deformed at 100° C in an inert atmosphere; these conditions reduced the influence of intermolecular reactions and prevented oxidation processes. Data on the tensile strength of various vulcanizates are recorded in Table 7; from these data it follows that resistance to repeated deformations under the conditions described is in general higher as the heat resistance of the vulcanization structures is greater. The Thiuram vulcanizates are an exception, in that they possess relatively low tensile strengths but have high heat resistance. Repeated deformation is accompanied by a decrease of the number of cross-links in the vulcanizate. Thus, besides the direct dependence of the behavior of vulcanizates on the stability of the vulcanization structures, the nature of the secondary processes which determine structural changes in the vulcanizates before they are destroyed is also of essential importance with respect to fatigue.

CONCLUSIONS

(1) The phenomenon of stress relaxation in vulcanizates, due to thermal decomposition of the vulcanization structures, is discussed. The process follows the equation: $\sigma_t = \sigma_0 \cdot e^{-kt}$, where k is the kinetic constant of decomposition of the vulcanization structures, and therefore can serve as a measure of the heat resistance of a vulcanizate.

(2) The amounts of polysulfide and disulfide bonds in various vulcanizates were determined.

(3) It is established that the heat resistance of vulcanizates depends on the total quantity and also on the proportions of bonds of the type: $R_1—C—C—R_2$, $R_1—C—S—C—R_2$, $R_1—C—S—S—C—R_3$, and $R_1—C—S_n—R_2$.

(4) It is shown that the relative contents of various vulcanization structures depends on the type of rubber and on the nature of the vulcanizing group. Thus, vulcanizates with tetramethylthiuram disulfide do not contain any polysulfide bonds, whereas vulcanizates with elemental sulfur (without accelerator) contain predominantly polysulfide bonds.

(5) It is established that recombination of the radicals formed during thermal decomposition of a vulcanizate leads to the formation of both intramolecular bonds and new stable bridge bonds.

(6) It is suggested that thermal decomposition of sulfur bridges is one of the causes of the phenomenon of a vulcanization optimum (reversion).

(7) A relation is established between the nature of vulcanization structures and the resistance of vulcanizates to repeated deformation.

REFERENCES

[1] Dogadkin and Reznikovskil, *Kolloid. Zhur.* **11**, 314 (1950).
[2] Flory and Rehner, *J. Chem. Physics* **11**, 521 (1943).
[3] Parker, *India-Rubber J.* **108**, 387 (1945).
[4] Armstrong, Little, and Doak, RUBBER CHEM. & TECHNOL. **7**, 788 (1944).
[5] Olsen, Hull and French, *Ind. Eng. Chem.* **38**, 1282 (1946).
[6] Craig, RUBBER CHEM. & TECHNOL. **24**, 262 (1951).
[7] Dogadkin, Karmin, and Stukalova, "Studies of the Physics and Chemistry of Rubbers", Moscow, **1950**, p. 59.
[8] Dogadkin, Bartenev, and Novikov, *Kolloid. Zhur.* **10**, 94 (1948).
[9] Dogadkin, "Studies of the Physics and Chemistry of Rubbers", Gov. Chem. Publ., **1950**, p. 21.

DISPERSION OF FILLERS IN RUBBER *

RUPRECHT ECKER

RUBBER AND SYNTHETICS DIVISION, FARBENFABRIKEN BAYER A.G., LEVERKUSEN, GERMANY

INTRODUCTION

The activity of a filler in rubber depends on the size and geometrical shape of the particles, and on their chemical constitution. The smaller a particle is, the larger is the total surface area of the filler per unit weight. If, for example, the diameter of a particle of an active carbon black is 30 mμ, the total surface area is about 100 sq. m. per gram. If the particle diverges from spherical shape and has a crystalline form, the surface area is greater, as the relation of the area of a sphere to that of a cube of equal volume clearly shows (surface area of sphere: surface area of cube = 12.5:15.6). Furthermore, corners and edges are present on a particle of crystalline shape, which are particularly active according to the experimental results of interface physics. By means of this phenomenon, the differing activity of various fillers of equal particle diameter can be explained.

THEORETICAL CONSIDERATIONS

If the rubber-filler system is considered from the standpoint of interface physics, the phenomena are analogous to those of chromatic adsorption[1]. In adsorption in solution, the solvent plays an essential role. In the rubber-filler system, the solvent, *viz.*, rubber, can be assumed to be practically invariable. On the other hand, the substance adsorbed, in our case the dispersing agent, the activator, or even the vulcanization accelerator, can change. This also explains why quite different mechanical values are found for a vulcanizate containing the same filler, but different accessory ingredients. It also follows from this that, because every filler differs from every other filler in its adsorptive properties, some particular activator is most effective for the particular filler. The term dispersing agent is really misleading; for, according to the results of our experiments, no substance aids directly in the dispersion of a filler. The dispersion of fillers in rubber is a secondary phenomenon in the use of the substances mentioned above. Bostrom[2], and also Morris and Hollister[3], came to practically the same conclusion in their studies of the effectiveness of fat acids in the dispersion of active carbon blacks in rubber. It would be more nearly correct to call these so-called dispersing agents bonding agents. The dispersion takes place mechanically at times; however, by the addition of so-called dispersing agents on a roll-mill or in an internal mixer, a union of rubber and filler takes place even during the mixing process. As a result, the whole system becomes harder, the mechanical friction is increased, and dispersion of the filler is enhanced. The strength of the bond between the adsorbed and adsorbing components, i.e., their adsorption affinity, called in brief their activity, is decisive in the appraisal of an adsorbent. While the process is reversible in the case of

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from *Kautschuk und Gummi*, Vol. 7, No. 5, pages WT 96-104, May 1954. This paper was presented at a meeting of the German Rubber Society, Goslar, May 7–9, 1953. An important part of the work was presented by E. Weinbrenner at a symposium on "Light Colored Reinforcing Fillers", in Vlotho, October 6–7, 1949.

chromatic adsorption, i.e., there is a separation of the adsorbed substance from the solvent, the process is irreversible in the case of a rubber-filler system, in which the adsorbed substance (activator or accelerator) is bound at the same time on the adsorbent (filler) and the solvent (rubber). In chromatic adsorption, one might say that the dispersing agent dissociates in the rubber.

The forces on the boundary surfaces between fillers and the surrounding rubber are obviously greater in the case of active fillers than the inherent strength of the rubber[4]; otherwise it would be impossible to explain the increase of tensile strength, strain modulus, and, above all, resistance to tearing. With inactive fillers, for example, ground whiting, the properties mentioned are poorer, because the binding forces at the boundary-surfaces are smallest for these substances and the rubber matrix is less in the cross-section of the test-specimen.

Smith[5] observed light phenomena in the rupture of thin films of rubber. These phenomena depend on the nature of the filler. With rapid stretching, only mixtures containing chalk, talc, and barytes (all inactive fillers), but not mixtures containing zinc oxide, titanium dioxide, or active gas blacks, show a light effect. Thus the active fillers, i.e., reinforcing fillers, behave fundamentally negatively. Presumably the rubber-filler bond is broken, whereby electrical changes appear and these occasion innumerable microdischarges inside the vacuoles present.

A study of Jones and Yiengst[6] on the effectivensss of stearic acid as a bonding agent between rubber and filler includes a noteworthy suggestion. In volumetric measurements in a dilatometer, unloaded rubber mixtures show a decrease of volume, whereas rubber-pigment mixtures show an increase of volume after stretching. The decrease of volume is related to the fibre development and orientation of the rubber molecules, while the increase of volume is attributed to a formation of vacuoles between the rubber and pigment surface. Most of the studies were made with zinc oxide. With increasing diameter of the particles of the zinc oxide pigment, the increase of volume of the rubber mixtures rises during stretching. In some cases this considerable increase of volume can be reduced greatly if sufficient stearic acid is added to the mixture. This is an indication that, with stearic acid, we are dealing not only with a dispersing agent but also with a binding agent.

FUNDAMENTAL BEHAVIOR OF ACTIVE AND INACTIVE FILLERS

EFFICIENCY OPTIMUM WITH RESPECT TO FILLER CONTENT

Before the question of the choice and development of effective activators is considered, the fundamental behavior of active and inactive fillers must be discussed insofar as it concerns the technologist concerned with various rubber mixtures. The optimum efficiency of fillers can be ascertained by studying the change of properties with degree of loading. Of course, the vulcanization conditions for each degree of loading must be so chosen that comparable degrees of vulcanization are obtained. If a diagram is constructed, with the properties plotted as the ordinate and the percentage of loading as the abscissa, e.g., percentage by weight, a progressive change of properties with the degree of loading of inert fillers is found almost throughout, whereas a maximum or minimum (according to the direction of the rating of the properties concerned) is found for active fillers. The location and height of this maximum or minimum on the curve are specific for individual active fillers, and will be known hereafter as the *efficiency optimum*. This optimum activity, or effectiveness, can be most suitably characterized by means of tensile strength, abrasion re-

sistance, resistance to tearing, and to a certain extent by the hardness. The lower is the degree of loading at which the optimum is reached, and the higher is the value of the efficiency optimum at its maximum or minimum point of efficiency, the more active a filler is to be considered.

Figure 1 shows a general comparison of the principal differences between active and inactive fillers. It is interesting that the efficiency optimum for the individual properties with the same filler does not correspond to the percentage loading; for example, the efficiency optimum can correspond to 30 per cent by weight of filler with respect to the tensile strength, and to 50 per cent by weight with respect to the resistance to tearing. It is also interesting that the efficiency optimum, with respect to the tensile strength and abrasion resistance

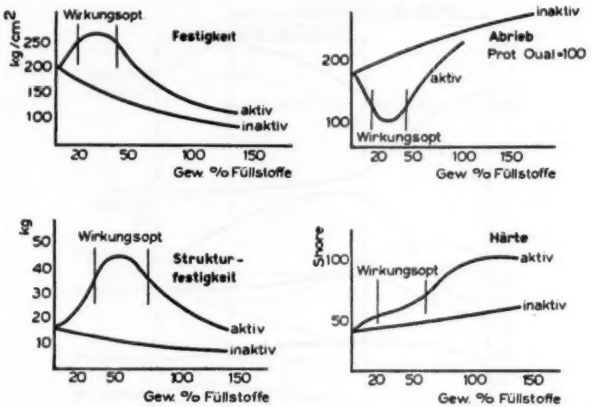


FIG. 1.—Comparative properties obtained with inactive and active fillers. In all four diagrams, the abscissa is the percentage by weight of the filler, and the pair of vertical lines show the efficiency-optimum range for the active filler. The diagrams are as follows: Top-left, tensile strength; Top-right, abrasion resistance; lower left, structural strength; lower right, hardness.

almost always appears at the same percentage loading. In the measurement of hardness, no very well-defined efficiency optimum is observed, but rather a tendency of the curve to flatten in the range of the efficiency optimum.

EFFICIENCY OPTIMUM WITH RESPECT TO INFLUENCE OF THE ACTIVATOR

In addition to the appearance of an efficiency optimum at a certain filler content, another efficiency optimum, which depends on the influence of the activator for a given constant filler content, can also be discerned. If the filler content in mixtures is kept constant, and the proportion of an activator particularly suitable for the filler is varied, it again appears that a definite optimum quantity of activator with respect to the quantity of filler is necessary in order to obtain optimum properties. The position of this second efficiency optimum depends on the nature of the activator used, and is specific with respect to the filler.

Hence another criterion for the characterization of active fillers becomes available. The important curves are shown in Figure 2. In this figure, various properties, such as tensile strength, abrasion resistance, hardness, modulus

at 400 per cent elongation, elasticity, and resistance to tearing, as related to the proportion of the activator, were plotted for a certain arbitrary filler loading.

In the systematic elaboration of such a system, it was again noteworthy that the optimum points of the individual properties are not the same for the same proportion of activator. The optimum resistance to tearing corresponds roughly with that of tensile strength, while the optimum hardness corresponds to the range in which optimum abrasion resistance and elasticity are located. From the course of the curves, one must conclude that two processes are superimposed in the development of this optimum, namely: (1) a process of activation of the filler by the activator, and (2) the influence of the activator present acting as a softener in the mixture. This effect is evident in the curves of

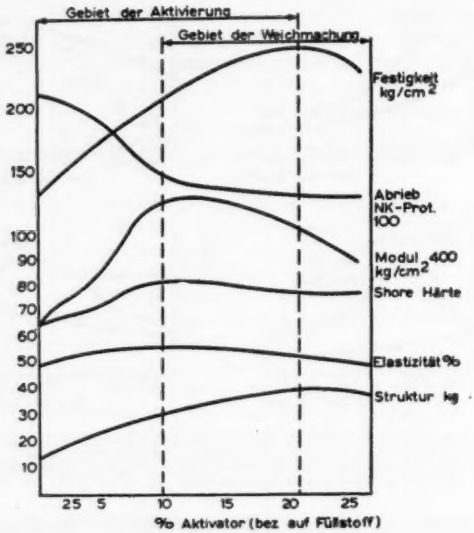


FIG. 2.—Influence of an activator on the properties, with constant filler content. The left ordinate scale represents all the properties designated on the right-hand ordinate. The abscissa is the percentage by weight of activator (based on the filler). The upper arrowed designation is the range of activation; below is the range of softening. The legends on the right-hand ordinate are (downward) the tensile strength, the abrasion reistance (referred to natural rubber base mixture = 100), the modulus at 400% elongation, the hardness, the percentage resilience, and the resistance to tearing.

modulus and hardness, which, after having reached the optimum, fall again at relatively low activator content. This phenomenon leads to the conclusion that a critical activator content is necessary to obtain optimum tensile strength. Any activator which is present in excess of this critical amount with respect to this property acts as a softener and causes a decrease of the value.

In Figure 3 the specific influence on the modulus of seven different substances used as activators is shown. With substance V, no optimum or minimum appears through the entire range of concentrations; substances VI and VII show no activating effect, and they are only effective softening agents throughout the range. Substances III and IV function as softeners at low concentrations and as activators only at higher concentrations; I and II are highly effective activators.

CHARACTERIZATION OF FILLERS AND ACTIVATORS

From what has been said in the last three sections, the characterization and evaluation of fillers or the investigation for suitable activators comprises the following technique:

(1) Determination of the efficiency optimum with respect to the filler.
(2) Determination of the efficiency optimum with respect to the activator.

At the same time, the purpose of such studies is to find activators which have an efficiency optimum, even at low concentrations, and which increase the activity of fillers over a wide quantitative range. For each proportion of filler, there is an optimum activator concentration and a most effective activator.

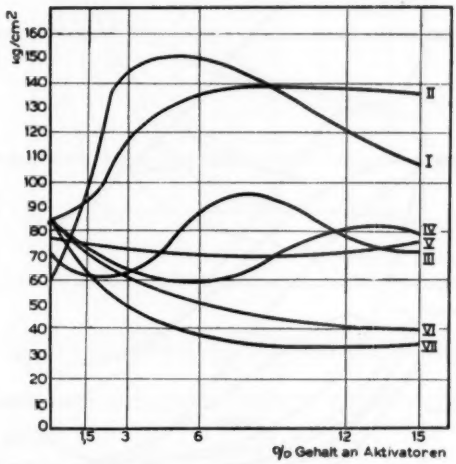


FIG. 3.—Specific effects of seven different activators on the modulus at 400 per cent elongation. The ordinate is the modulus; the abscissa is the percentage of activator.

By means of what properties, then, can activators and reinforcing fillers be suitably characterized?

The characterization of reinforcing fillers by means of the properties of vulcanizates containing them has just been discussed. However, the manufacturer is also interested in the behavior of reinforcing fillers during the mixing process.

CHARACTERIZATION OF FILLERS IN UNVULCANIZED MIXTURES

For the various intended uses and processing techniques involved in the production of finished articles, the stiffness of the mixtures and (or) the degree of plasticity is sometimes necessarily restricted. Accordingly, the extent to which different types of mixtures can be loaded with reinforcing fillers is also limited for technologists. It has become a generally recognized fact that highly active fillers have an extraordinarily distinctive effect on unvulcanized mixtures[7]. Consequently, a good knowledge of the behavior of the individual products in unvulcanized mixtures, as well as their effects on the properties of vul-

canizates, is essential. Furthermore, in formulating mixtures, it is necessary to choose favorable and optimum combinations for the particular uses from the wealth of possibilities.

In Figure 4 the Defo hardness, measured in systems of 60 parts by weight of filler in 100 parts by weight of rubber, and activated by 1.5 to 15 per cent of an activator, which was experimentally developed and is hereafter designated as Akticit-A, is illustrated. As Figure 4 shows, in the mixtures tested, Defo hardnesses between 250 and 4500 were obtained for various light-colored reinforcing fillers in equal concentrations. One is not justified in judging the use-

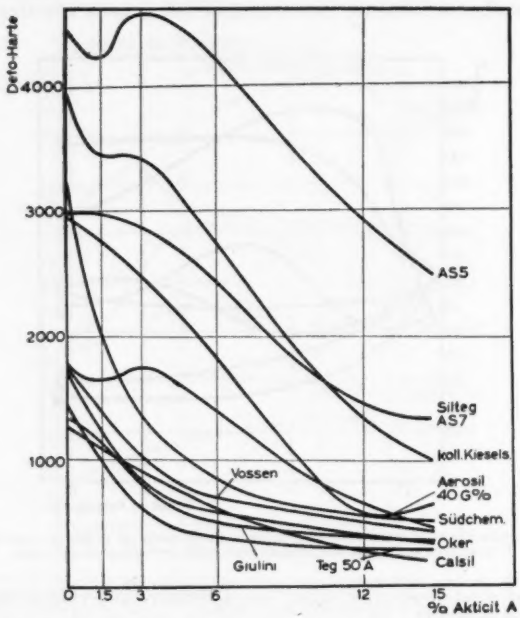


FIG. 4.—The plasticity of unvulcanized mixtures containing the same activator, but different light-colored reinforcing fillers. The ordinate is the Defo hardness; the abscissa is the percentage of Akticit-A.

fulness or degree of activity of a filler directly from the Defo hardness of the vulcanizate. The figure serves only to show how different are the effects of different fillers in rubber mixtures, and, with respect to processability, that the amount of filler which can be added is limited. There are, in fact, cases where, because of stiffening of the unvulcanized mixture, the loading must be below that required to obtain the optimum properties after vulcanization.

In Figure 4, the relations for an individual activator with various light-colored reinforcing fillers are illustrated. Figure 5 in turn shows the influence of various common commercial activators in mixtures containing the same filler (Teg) on the plasticity of the crude mixtures. The mixtures were again compounded like those in Figure 4.

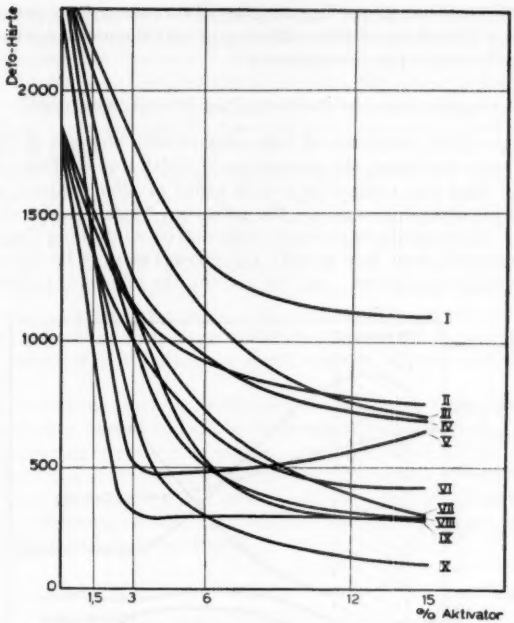


FIG. 5.—Hardness of unvulcanized mixtures containing the same content of filler (Teg), but ten different activators. The ordinate is the Defo hardness; the abscissa is the percentage of activator.

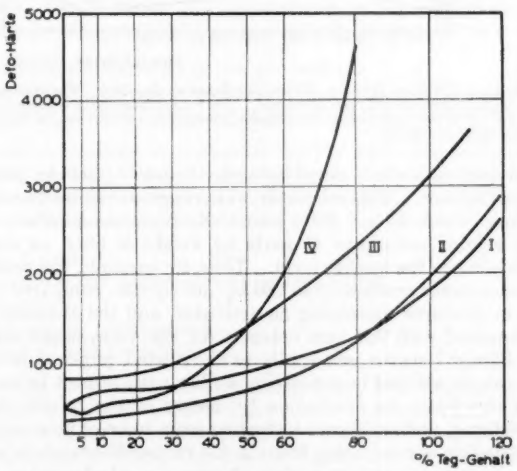


FIG. 6.—Plasticity of mixtures containing various types of Teg filler. The ordinate is the Defo hardness; the abscissa is the percentage of Teg.

In Figure 6, various types of Teg are plotted for comparison, in order to show that important differences in the stiffening of unvulcanized mixtures may be found within the same type of substance.

CHARACTERIZATION OF FILLERS IN VULCANIZATES

The change of the properties of vulcanizates with changes of filler content when an activator is present, the proportion of which was so chosen that a relatively optimal dose was assured in a wide range of filler content, is shown in Figure 7. In the foregoing example, the activator, Akticit-A, mentioned above was used, and the range of properties of vulcanizates containing Teg were determined. The results show how greatly the properties may be changed by the addition of suitable activators. In this system, the efficiency optimum for the

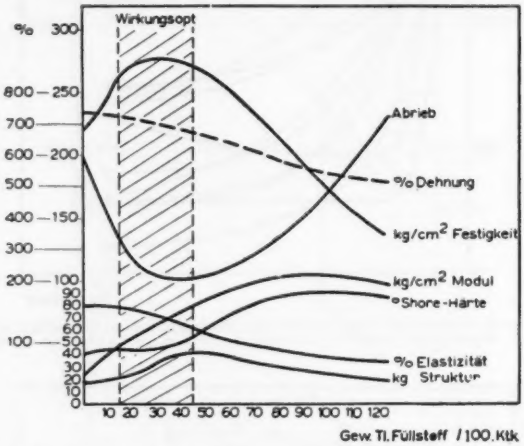


FIG. 7.—Activation of Teg by Akticit-A (12 per cent, based on the filler). The abscissa represents the parts by weight of filler (based on 100 parts of rubber). The shaded range is the efficiency-optimum range. The legends of the curves are (downward) the abrasion, elongation, tensile strength, modulus, hardness, resilience, and resistance to tearing.

important properties lies in a range between 15 and 45 parts by weight of filler to 100 parts of rubber. This relatively wide range comprises the optimum attainable values, which do not differ essentially from one another, while below 15 parts by weight, and above 45 parts by weight of filler, an extraordinary change takes place in the quality level. Thus, for example, the tensile strength in this efficiency range reaches up to 280 kg. per sq. cm., compared with 220 kg. per sq. cm. in mixtures containing no activator, and the abrasion is 100 unit volumes, compared with 200 unit volumes for the vulcanizate containing no activator. Figure 7 serves principally to show what physical properties of a vulcanizate can be utilized in evaluating a filler with respect to its reinforcing action. On this basis, an evaluation by means of the tensile strength, the abrasion resistance, and resistance to tearing seem to be of most significance.

If the activation of reinforcing fillers in the rubber-filler system is considered from the standpoint of boundary-surface physics, e.g., of adsorption, it is evident that in addition to activation of the filler, there is an accompanying activation

of the vulcanization process. Otherwise it can not be explained why the addition of ethyleneglycol as a filler activator accelerates at the same time the vulcanization process. In the case of ethyleneglycol, the accelerating action can be explained by the fact that the glycol occupies the active points of the filler during the mixing process, so that, in the extreme case, no more accelerator can be adsorbed, and consequently the accelerator remains quite free to exert its full accelerating action.

On the other hand, a strong activation of the filler results when the amount of accelerator is increased above the usual maximum proportion, since all vulcanization accelerators, because of their chemical composition, and thus their polar properties, are adsorbed on interfacially active substances. In the opinion of the author, the better dispersion of the filler is, as has already been mentioned, a secondary phenomenon. Consequently, a careful study, first, of the tendency to prevulcanization, second, of the complete vulcanization process and third, of the level of the properties obtained after complete vulcanization, including the vulcanization plateau, is recommended for the appraisal of fillers and activators.

All these questions must be settled for every degree of loading and every degree of activation, here, too, the disadvantage of a single effect often prevents the degree of loading necessary to obtain a certain desired property in the vulcanizate, so that one is forced, in technical work, to attain the desired effect by special combinations of active and inactive fillers, always taking into account the maximum stiffening of the unvulcanized mixture which can be tolerated from a practical processing standpoint.

ACTIVATORS

The rubber section of the Farbenfabriken Bayer A.-G. at Leverkusen has devoted itself, in a very comprehensive series of investigations, to the problem of determining the most effective classes of substances and studying thoroughly their suitability as activators for light-colored reinforcing fillers. The substances have been characterized from the following points of view:

1. Efficiency optimum when in low proportions.
2. Attainment of high tensile strength, with, at the same time, good abrasion resistance, and good resistance to tearing of the vulcanizate.

The individual substances were studied, by the operating technique already described, with a view to determining the dependence of the properties of the vulcanizates on the filler content and activator content. The following classes of effective substances were found:

(a) Organic acids
(b) Ammonium and amine salts of organic acids.
(c) Acid amines.
(d) Metal salts of organic acids.
(e) Dialcohols and aminoalcohols.

The following facts which were established may be of interest in connection with a possible theoretical interpretation. (1) The best effect was obtained with dipolar compounds containing similar or equivalent groups. (2) With respect to hydrophilic fillers, the most effective activators are those which possess a hydrophilic constituent with an affinity for the filler and a rubber hydrocarbon-soluble constituent. To the first qualification can be added the

fact that the dipole moment is not the only characteristic that plays an important role. This is a necessary but still insufficient requirement. The polarizability also is of essential importance, as in chromatic adsorption. The importance of polarizability can be demonstrated convincingly by the isomers of dinitrobenzene. In one mixture, consisting of 100 parts by weight of rubber, 60 parts of Teg, and 6 parts of dinitrobenzene as activator, and the usual vulcanization agents (zinc oxide, sulfur, accelerator), the vulcanizates gave the values shown in Table 1.

TABLE 1

	Tensile strength (kg. per sq. cm.)	Modulus at 400% (kg. per sq. cm.)	Shore hardness	Resistance to tearing	Abrasion loss (% vol.)
No addition	148	73	57	12	202
1,2-Dinitrobenzene $\mu = 6.0$ D	204	135	67	37	155
1,3-Dinitrobenzene $\mu = 3.77$ D	183	102	63	26	146
1,4-Dinitrobenzene $\mu = 0$ D	207	129	67	31	153
Dodecylbenzene $\mu = 0$ D	120	50	48	12	248

Although 1,4-dinitrobenzene has the dipole moment zero, as does dodecylbenzene, the former has a strong activating effect on the filler. In the case of 1,4-dinitrobenzene, however, a very unstable equilibrium of the dipole moment can be assumed, and this may be disturbed by the slightest change of field; on the other hand, in the case of dodecylbenzene, the dipole moment is in stable equilibrium. This substance acts only as softener in the unvulcanized mixture and in the vulcanizate.

The relations become considerably more complicated and obscure if dissimilar substituents are present in the molecule, as is shown for the example of benzoic acid.

TABLE 2

	Tensile strength (kg. per sq. cm.)	Modulus at 400% (kg. per sq. cm.)	Shore hardness	Resistance to tearing	Abrasion loss (% vol.)
No addition	148	83	57	12	202
Benzoic acid	205	111	76	37	147
2-Nitrobenzoic acid	165	90	74	25	169
4-Nitrobenzoic acid	117	69	68	8	213
Dinitrobenzoic acid	129	63	54	9	201
Dichlorobenzoic acid	226	90	66	37	196
3-Nitro-4-chlorobenzoic acid	111	54	57	9	200

Here too, the substances are polar in every case, nevertheless, the effect is quite different, in part even negative. The polarizability also appears as an important factor, besides the dipole moment. Furthermore, the acid number of the substance is very important, as can be demonstrated by the example of Fischer, Tropsch, and Gatsch (see Table 3).

The fat acids were adjusted to neutrality with ammonia. The three series of experiments give only an approximate idea of the physical and chemical properties which are essential to the effectiveness of various substances as acti-

vators. A complete explanation of the more complicated processes and relations has not yet been offered.

The following considerations, based on the experiments, should be pointed out as technically important and effective principles:

(1) The activation of hydrophilic fillers containing water by activators which bind the water adsorptively or as emulsions;

(2) Activators, which act as dehydrating agents of the filler.

TABLE 3

	Tensile strength (kg. per sq. cm.)	Modulus at 400% (kg. per sq. cm.)	Shore hardness	Resistance to tearing	Abrasion loss (% vol.)
No addition	148	73	57	12	202
Acid number: 0	78	43	53	6	300
Acid number: 78	161	72	53	20	230
Acid number: 96	202	62	57	30	113
Acid number: 121	231	87	60	32	148
Acid number: 193	217	91	71	33	150
Acid number: 303	211	115	80	36	167

Considering all technical and theoretical problems, and bearing in mind that all the effects can not yet be fully explained, we developed an activator combination, already mentioned under the name "Akticit-A", for the purpose of studying light-colored reinforcing fillers. The objectives in the development of this byproduct were:

1. To diminish the tendency of fillers to stick to the mixing rolls and internal mixer blades;
2. To avoid a too great stiffening effect in unvulcanized mixtures;
3. To obtain efficient dispersion of the filler;
4. To obtain the highest qualities in the vulcanizate.

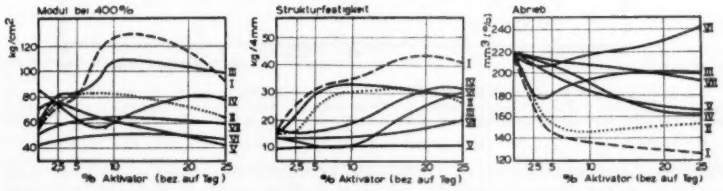


FIG. 8.—Effects of different activators with Teg as filler. I. Akticit-A. II. Stearic acid. The abscissa of the three diagrams represents the percentage of activators (based on the filler). The three diagrams are, from left to right, the modulus at 400% elongation, the abrasion, and the resistance to tearing.

Figure 8 shows a comparison of various activating substances with Akticit-A. As is seen by this comparison, the highest values could be obtained by the use of Akticit-A, for example with Teg, compared with other likewise good "dispersing agents". In addition to the investigations to obtain the best physical values with light-colored reinforcing fillers, other fillers, in some cases inactive, were also tested in the rubber-Akticit-A system. As Figure 9 reveals, it was established that efficiency optima also appear with other fillers. Caution is therefore needed in any one-sided discussion of absolute values in the consideration of light-colored reinforcing fillers. Quite remarkable effects may be ob-

served in the increase of tensile strength and improvement of abrasion resistance by the use of certain substances and combinations of substances, such as Akticit-A, with other products hitherto not considered to be reinforcing fillers.

THE VULCANIZATION PROBLEM

As promising as the general properties of vulcanizates containing light-colored reinforcing fillers seem to be, as has been systematically established by the use of suitable activators, an explanation of these phenomena is very difficult, particularly when they are considered together with the problem of vulcanization and vulcanization acceleration. Thornhill and Smith[8] studied the effect of reinforcing pigments on the rubber hydrocarbon in simple rubber-sulfur mixtures and in mixtures containing accelerators, and found the expected decrease of the number of double bonds. On the other hand, mixtures containing

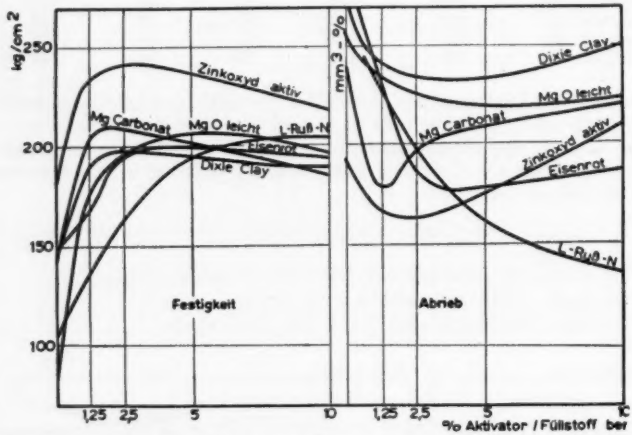


FIG. 9.—Dispersion of various fillers by Akticit-A. The abscissa represents the percentage of activator (based on the filler). The left-hand diagram is Tensile strength; the right-hand diagram is the abrasion. On the diagram, *Russ* signifies *carbon black; Eisenrot, red iron oxide.*

active carbon black showed no change in the degree of saturation. They concluded that this was related to an orientation of the rubber molecules, which is caused by the reinforcing fillers, and that the union of sulfur to the rubber hydrocarbon takes place at other points of the rubber molecule. More recent experimental observations of the effect of vulcanization accelerators assume that only nucleophilic substances are effective accelerators[9], i.e., substances which are able to attack both sulfur and the rubber molecule, and thereby to cause electron displacements in both cases, so that points other than the double bonds are formed as active centers for the linking of the sulfur-rubber molecules. Similar conditions must also be assumed for the bonding of pigments to rubber through the agency of suitable activators. Thus it would be incorrect to regard rubber as a pure hydrocarbon. Every rubber, natural or sunthetic, carries a thin film of protective colloids after precipitation from its latex, which promotes union with most polar fillers. Thus, Martin[10] found that highly purified rubber, in

which most of the film had been removed, required larger quantities of stearic acid. A similar effect was established in studies concerned with thorough washing of fillers. The experiments were carried out with Teg. This filler was washed with distilled water several times and dried at 150° C. When the washed and redried filler was mixed with rubber and the product vulcanized, the physical properties of the vulcanizate showed a well-defined dependence on the extent of washing, in the sense that, with increasing extent of washing of the Teg, the attainable physical values became progressively poorer, as is evident in Figure 10. This is particularly evident for the abrasion resistance and ten-

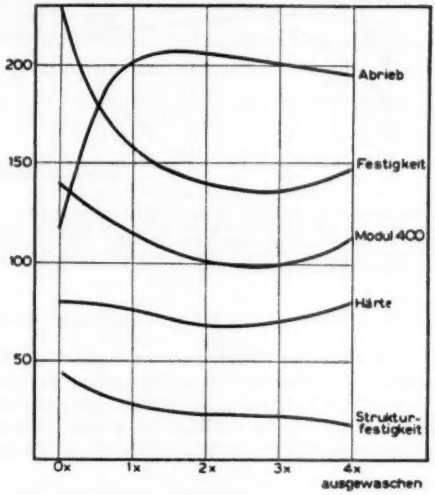


FIG. 10.—Effect of washing of Teg on the properties of vulcanized rubber-Teg mixtures. The ordinate values are for all the properties noted on the right-hand ordinate. The abscissa represents the number of washings.

sile strength, in which cases, after a single washing, the values were only those obtainable with nearly inactive products. As is known, Teg is a strongly hydrophilic filler, which contains a large amount of bound water as marketed. This water appears to have the function of protecting the active points on the surface of the Teg. During the mixing process, this bound water is partially replaced by the more highly polar activator, as a result of which the liberated water passes off as vapor. This phenomenon also indicates the effectiveness of water as an activator in Teg. Thus Schneider[11] found, by adding water to the mixtures, pronounced efficiency optima, which differed greatly among individual fillers, as the following comparison shows:

TABLE 4

Product	Efficiency optimum
Teg (Oker)	60–70% water
Teg (Giulini)	50–60% water
AS-5	>70% water
Calsil	30–40% water

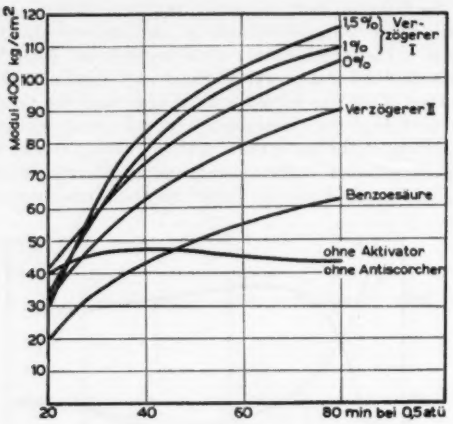


FIG. 11.—Prevulcanization with Teg as filler. Effect of antiscorching agents. The base mixture was: rubber 100, Teg 60, and Akticit-A 8 parts. The ordinate is the modulus at 400 per cent elongation; the abscissa is the time in minutes of heating at 0.5 atmospheres' pressure. The top three curves are for retarder I, the curve below is for retarder II, the still lower curve is for benzoic acid, and the bottom curve is for a mixture containing no activator or antiscorching agent.

INFLUENCE OF ZINC OXIDE IN VULCANIZATION WITH TEG

If active zinc oxide is added to light-colored reinforcing fillers, an increase of the physical values of the filler exceeding the normal level takes place. This is, in particular, the case if activating substances are also added. A further large increase of the values can be obtained by greatly increasing the dose of accelerator in the presence of zinc oxide as additive to the light-colored reinforcing filler.

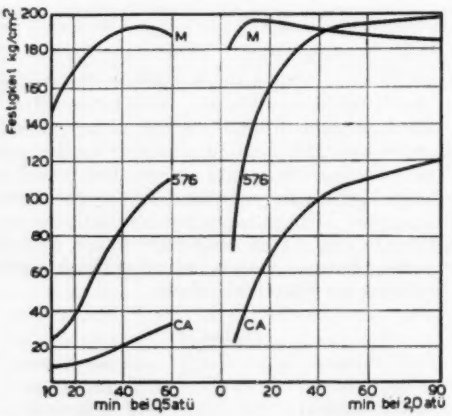


FIG. 12.—Vulcanization with different vulcanization accelerators and with Teg as filler: The ordinate is the tensile strength; the abscissa is the time of heating at 0.5 and 2.0 atmospheres' pressure.

PREVULCANIZATION WITH LIGHT-COLORED REINFORCING FILLERS

Many mixtures prepared with light-colored reinforcing fillers tend toward prevulcanization. This tendency is increased if combinations of substances are used which activate both the filler and the vulcanization process. Akticit-A offers such a combination. This product was developed in order to obtain the maximum effect of the individual reinforcing fillers in improving the physical properties after vulcanization. In systems activated in this way, and which tend to prevulcanized, the danger of scorching can not be reduced simply by the addition of vulcanization retarders (anti-scorching agents). The danger of scorching can, however, be greatly retarded in these systems, if benzoic acid is

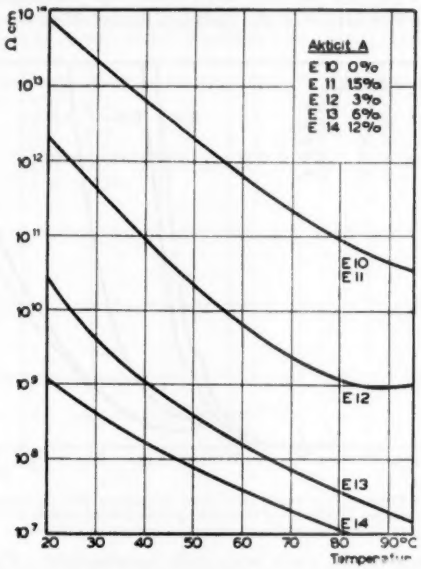


FIG. 13.—Specific electric resistances of mixtures containing different light-colored reinforcing fillers and increasing proportions of Akticit-A.

added to the mixture in an amount roughly equal to the amount of Akticit-A, and this does not impair the physical properties of the vulcanizates. In Figure 11 these relations are illustrated graphically.

INFLUENCE OF VULCANIZATION ACCELERATORS

If rubber containing basically reacting light-colored reinforcing fillers is vulcanized with acidic accelerators, there is a considerable increase of the rate of vulcanization and, consequently, a greatly increased danger of scorching. In Figure 12, several characteristic curves of basic and acidic accelerators in a rubber-Teg-Akticit-A system are compared. It is clearly seen that it is quite possible, by the use of basic accelerators, to control the basic-reacting system without great danger of scorching, whereas the control of vulcanization with

acidic vulcanization acceleration is difficult or altogether impossible. One is forced to conclude that the basic character of the filler or activator has the effect of adding a basic double accelerator to the acidic accelerator, and that it is necessary to take this into account in formulating mixing recipes for the successful use of light-colored reinforcing fillers.

Based on the foregoing results, it can be stated unequivocally that the activation of light-colored reinforcing fillers is, in a similar manner, a vulcanization problem. Despite all the difficulties from a technical viewpoint which are to be expected in the processing of mixtures containing light-colored reinforcing fillers, these difficulties can be overcome by suitable mixing recipes. With active fillers composed essentially of colloidal silicic acid, e.g., Aerosil, Vulkasil-S, and Ultra-Silteg VN3, the behavior with respect to prevulcanization is not so unfavorable, since the nature of the products is such that they do not increase

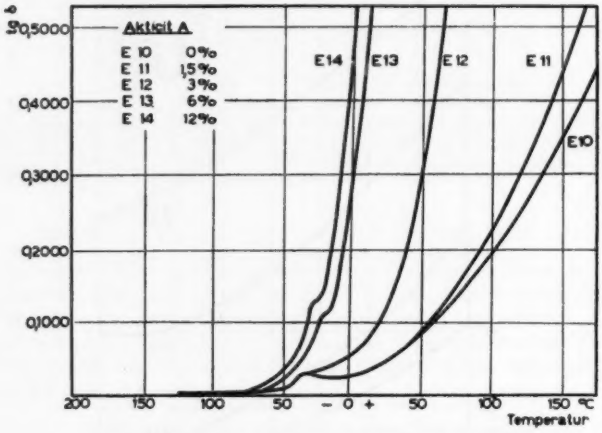


FIG. 14.—Dielectric loss angles of mixtures containing different light-colored reinforcing fillers and increasing proportions of Akticit-A.

the rate of vulcanization, even with acid acceleration. Consequently, the mixtures are easier to control. In order to obtain the full effect of such products on the physical properties of the vulcanizates, a relatively high percentage of vulcanization agent is necessary, according to earlier experiments, and the use of auxiliary products of the type of Akticit-A appears to be quite satisfactory for colloidal silicic acid, since these fillers tend much more to retard than to accelerate vulcanization[12].

LIGHT-COLORED REINFORCING FILLERS AND THE DIELECTRIC PROPERTIES OF VULCANIZATES

If increasing quantities of an activating polar agent of the type of Akticit-A are added to a base mixture consisting of 100 parts of natural rubber and 60 parts by weight of Teg, the specific resistance at all temperatures above 20° C decreases and reaches the order of magnitude of a semiconductor at 6 parts by weight (based on the rubber content). The changes of the loss angle and dielectric constant are analogous, as is evident from Figures 13, 14, and 15. It is

thus possible to prepare semiconductive mixtures, as is so often desired. For good insulating cable mixtures, however, such combinations should be used with caution.

LIGHT-COLORED REINFORCING FILLERS COMPARED WITH ACTIVE CARBON BLACKS

The problem involved in the use of light-colored reinforcing fillers can not be compared simply with the problem of "white carbon black". Considering the properties of the light-colored reinforcing fillers, it is well, first of all, to discuss them in a general way from the viewpoint of improving otherwise inactive or semiactive fillers. The latter have proven their usefulness along with carbon blacks, without being able to any extent to break into the fields of use of carbon black. Thus, in the substitution of carbon black by an equivalent light-colored filler, conditions are involved which would not be directly suitable for the im-

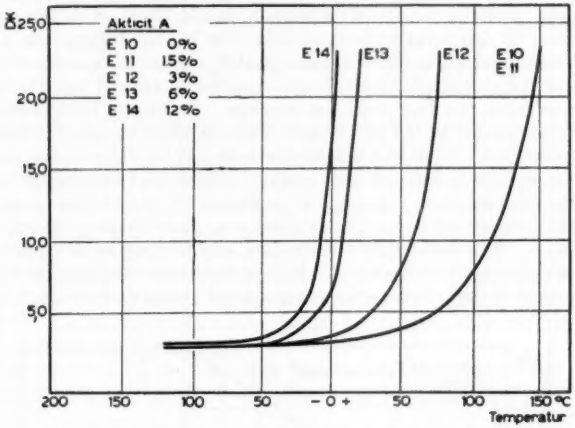


FIG. 15.—Dielectric constants of mixtures containing different light-colored reinforcing fillers and increasing proportions of Akticit-A.

proved filler. Consequently, in order to develop products under the label "white carbon black", the demands which such a product must meet in order to be regarded as "white carbon black" should first of all be defined.

For example, a "white carbon black" must, first of all, combine all the positive properties which heretofore have been peculiar to carbon black, both from the quality and the economic viewpoints. In addition, it would be desirable to improve certain properties. In this connection, for example, there comes to mind the decrease of the loss of elasticity with increasing degree of loading and the ensuing improvement of heat build-up under dynamic stress.

Mixtures formulated correctly on the principle of efficiency optima and vulcanized properly with light-colored reinforcing fillers are, as far as abrasion resistance, tensile strength, and resistance to tearing are concerned, comparable in quality to corresponding mixtures containing active carbon black. This is exemplified in Table 5.

A comparison of the resilience shows the superiority of the mxitures loaded with light-colored reinforcing fillers over those containing active carbon blacks.

TABLE 5

	Tensile strength (kg. per sq. cm.)	Resistance to tearing	Abrasion
Carbon-black tire tread	260–280	48	100
Teg tire tread	240–260	45	120
Aerosil tire tread	280–300	55	120

The object of obtaining improved resilience with no loss of abrasion resistance or resistance to tearing can be considered attainable on the basis of previous observations. Thus, some day the introduction of light-colored reinforcing agents into the domain where only active carbon black mixtures have heretofore been used (tires, conveyor belts, etc.) is quite possible. Since, however, not only the elastic behavior, but also other properties, e.g., fatigue and breakdown resistance, to mention only two, are of decisive importance in dynamically stressed particles, particular attention should be given to these factors.

In Figure 16 comparative fatigue data (De Mattia fatigue) on a carbon-black tire tread and a Teg tire tread are plotted. Here the quality at low temperatures of the carbon-black tread was superior to that of the Teg tread; at high temperatures, the Teg tread was superior. Naturally further comparison of the relative quality of the two treads could be made by other corresponding tread formulations. Thus the Martens fatigue test for vulcanizates containing 60 parts by weight of Teg per 100 parts of rubber and containing increasing proportions of Aktacit-A, reproduced in Figure 17, shows how greatly, with light-colored reinforcing fillers, the activation and acceleration effects influence the resistance. This test demonstrates that, with increasing activator content, the fatigue resistance increases, and a fatigue resistance is attainable which is at least the equal of that of correctly compounded active carbon-black mixtures.

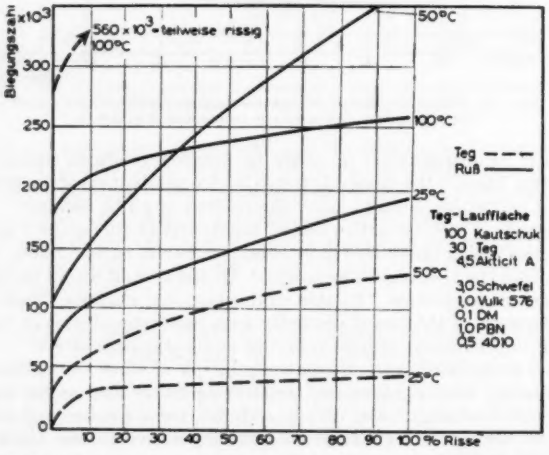


FIG. 16.—De Mattia fatigue values of tire treads containing carbon black and Teg, respectively, and tested at different temperatures. The ordinate is the bending angle; the abcissa is the percentage cracking. The upper-left curve represents partial cracking. The solid curves represent carbon-black mixtures; the broken curves Teg mixtures.

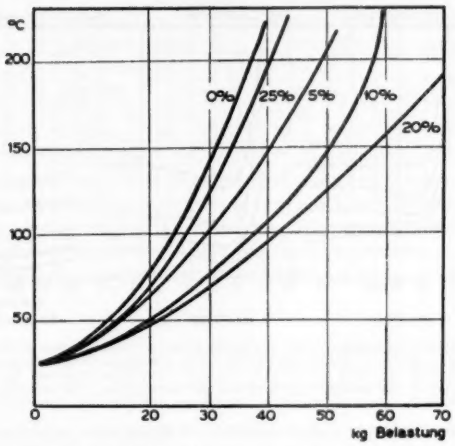


FIG. 17.—Breakdown, by the Martens test, of mixtures containing 60 parts of Teg per 100 parts by weight of rubber and increasing percentages of Akticit-A. The abscissa is the load in kg.

While the properties described above offer an extremely optimistic prognosis, various disadvantages stimulate interest in the improvement of light-colored reinforcing fillers. Among these drawbacks are variable yields from batch, particularly among the individual Teg products; bad light-aging, the excessive hardness of some unvulcanized mixtures; the strong tendency of different reinforcing fillers to cause prevulcanization during processing, for example, during extrusion and calendering operations, and the tendency to adhere to the rolls during milling.

Another condition is so important that a further study of the problem is necessary, namely, the problem of permanent deformation after static and

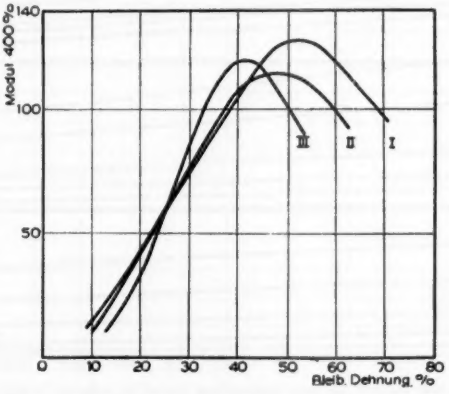


FIG. 18.—Elastic-plastic properties of mixtures containing various types of Teg. The ordinate represents the modulus at 400 per cent elongation; the abscissa the percentage permanent deformation.

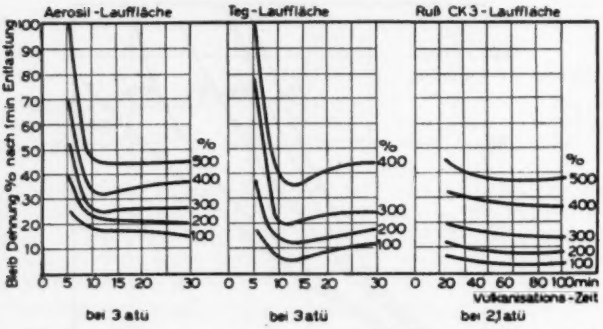


FIG. 19.—Permanent deformation, after having been loaded for 1 minute, of tire-tread mixtures containing Aerosil, Teg, and carbon black, respectively. The ordinate is the percentage permanent deformation after subjection of the mixtures to a load for 1 minute; the abscissa represents the time of vulcanization in minutes at 3, 3, and 2.1 atmospheres' pressure for the Aerosil, Teg, and carbon black mixtures.

dynamic tensile stress or compression. If the strain modulus is plotted as a function of the permanent elongation of vulcanizates containing, for example, various types of Teg, at, for example, 400 per cent elongation (see Figure 18), it will be found that the individual types of Teg show differing behavior with respect to the functions enumerated. If the values of the permanent deformation, which are plotted against the individual modulus values, are examined, it is evident that the permanent deformation is very high compared with that of carbon black mixtures. This phenomenon is observed not only with Teg, however, but with practically all light-colored reinforcing fillers. Mixtures containing light-colored reinforcing fillers, but no activator, manifest a quite

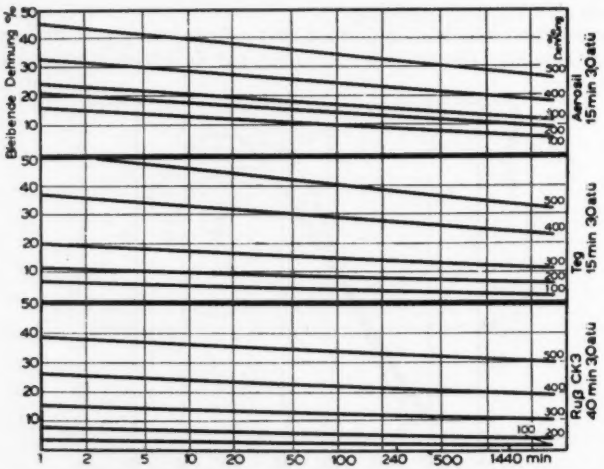


FIG. 20.—Permanent deformation, after having been loaded for different lengths of time, of tire-tread mixtures containing Aerosil, Teg, and carbon black, respectively. The left-hand ordinate gives the percentage permanent deformation; the right-hand ordinate the percentage elongation for the three mixtures indicated; the abscissa the time in minutes under load.

normal behavior with respect to permanent deformation. On the contrary, the permanent deformation increases with increasing activator content, irrespective of type, just as with mixtures containing no activator but containing abnormally high proportions of vulcanization accelerators.

This phenomenon can not be avoided altogether even by adjustment and operating technique of the vulcanization process. In Figures 19 and 20 the relations are plotted graphically for carbon black, Teg, and Aerosil tire-tread vulcanizates. This phenomenon stands in apparent contradiction to the experimentally established fact of improved rebound resilience. In an experimental testing procedure like dynamic damping, in which the compression stress is nullified by a corresponding tensile stress, heat build-up is, nevertheless, observed as a result of the two-fold internal friction process, so that this apparent contradiction can be explained accordingly.

REFERENCES

[1] Timm and Scheele, "The Relation between the Activity and the Adsorption of Dyes by Powder Dispersoids", paper presented at a symposium on "Light-Colored Reinforcing Fillers", in Vlotho, September 22, 1948.

[2] Boström, "The Dispersion and Absorption of Light-Colored Reinforcing Fillers", paper presented at a symposium on "Light-Colored Reinforcing Fillers", in Vlotho, October 6–7, 1949. See also *Kautchuk u. Gummi* **3**, 443 (1950).

[3] Morris and Hollister, *Ind. Eng. Chem.* **40**, 2325 (1948).

[4] Cohan, *India Rubber World* **117**, 343 (1947).

[5] Van Rossem, *Proc. 2nd Rubber Technol. Conf. London*, **1948**, p. 345.

[6] Jones and Yiengst, *Ind. Eng. Chem.* **32**, 1354 (1940).

[7] Krug, *Kautschuk u. Gummi* **5**, WT 72 (1952); Fromandi and Ecker, *Kautschuk u. Gummi* **5**, WT 191 (1952); **6**, WT 6 (1953).

[8] Thornhill and Smith, *India-Rubber J.* **103**, 214 (1942).

[9] Van Alphen, *Rev. gén. caoutchouc* **27**, 529 (1950).

[10] Martin, *Proc. 2nd Rubber Technol. Conf. London*, **1948**, p. 319.

[11] Weinbrenner, "The Influence of the Moisture Content on the Dispersibility and the Quality of Light-Colored Reinforcing Fillers", paper presented at a symposium on "Light-Colored Reinforcing Fillers", in Vlotho, September 22, 1948.

[12] Ecker, *Kautschuk u. Gummi* **5**, WT 171 (1952).

POLYMERIZATION PHENOMENA IN THE VULCANIZATION PROCESS *

B. Dogadkin, M. Feldsteĭn, A. Dobromyslova, V. Shkurina, and M. Kalpunov

M. V. Lomonosov Fine Chemical Technological Institute, Moscow, USSR

According to theories developed by the authors[1], vulcanization consists essentially in the formation of local chemical van der Waals bonds (polarization, orientation bonds) and hydrogen bonds between the molecular chains of rubber. These bonds are formed as a result of the chemical reaction of the rubber with the vulcanizing agent, oxygen, and accelerators, and with other components of the vulcanizing system which contain functional groups. The essential type of chemical bonds consists of atomic groups of the vulcanizing agent (in the case of sulfur vulcanizates, "bridge" sulfur). Hypotheses were advanced concerning the course during vulcanization of the polymerization processes, initiated by the free radicals which are formed by the vulcanizing agent, and leading to the formation of $-C-C-$ bonds between the molecular chains of the rubber. However, no proof of the existence of such processes has been obtained; furthermore, certain data, for example, data obtained by spectral analysis, contradict such an assumption. The present paper is devoted to a description of experiments which show the existence of polymerization processes involving free radicals in vulcanized systems which contain accelerators of the disulfide and sulfenamide type.

Dogadkin and Feldsteĭn discovered the vulcanizing action of benzothiazolyl disulfide and benzothiazolesulfendiethylamide when different types of rubbers containing these compounds are heated at 143° C. The vulcanizing action depends on the type of rubber; it is least manifest in the case of natural rubber; benzothiazolyl disulfide acts most intensively on sodium-butadiene rubber and benzothiazolesulfendiethylamide on butadiene-styrene rubber.

The dynamics of the change of tensile strength and permanent deformation, during heating, of a sodium-butadiene rubber mixture containing 50 parts by weight of channel carbon black and 5 parts of dibenzothiazolyl disulfide per 100 parts of rubber, and a similar mixture containing 2 parts of sulfur are shown as examples in Figure 1. As is seen, benzothiazolyl disulfide has a stronger vulcanizing action in this case than the conventional vulcanizing agent, sulfur.

Inasmuch as heating of benzothiazolyl disulfide and benzothiazolesulfendiethylamide does not cause liberation of elemental sulfur, it may rightfully be assumed that vulcanization in this case is a final result of decomposition of the compounds indicated into free radicals, which cause polymerization of the rubber hydrocarbon. This assumption is confirmed by the fact that a vulcanizate contains chemically bound sulfur and nitrogen which are not eliminated by prolonged extraction with acetone. These elements can enter the molecular chains only in the form of radicals formed from the compounds mentioned. As is seen from Table 1, up to 45 per cent of benzothiazolesulfendiethylamide enters into the reaction with rubber during heating for a period of 200 minutes.

* Translated for Rubber Chemistry and Technology from *Doklady Akademii Nauk SSSR*, Vol. 92, No. 1, pages 61–64 (1953).

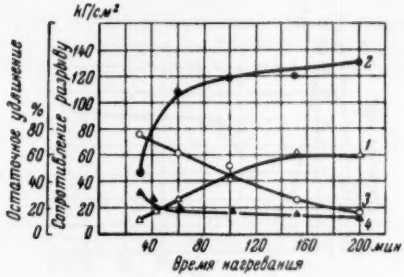


FIG. 1.—Changes of tensile strength by heating mixtures of sodium-butadiene rubber and carbon black containing (1) sulfur and (2) benzothiazolyl disulfide. The changes of residual elongation are represented correspondingly by curves (3) and (4). The abscissa represents the *Time of heating in minutes*; the left-hand ordinate the *Percentage residual elongation*, and the right-hand ordinate the *Tensile strength in kg. per sq. cm.*

The relation of the modulus of a vulcanized mixture to the proportion of reacted benzothiazolesulfendiethylamide (Figure 2) is represented by a straight line; this is in quantitative agreement with contemporary theoretical concepts, according to which the modulus is a linear function of the number of cross-links between the molecular chains of a vulcanizate. This means that, in the process described, the number of cross-linkages of the rubber molecules is proportional to the number of molecules of benzothiazolesulfendiethylamide which react.

TABLE 1

QUANTITY OF BENZOTHIAZOLSULFENDIETHYLAMIDE (PERCENTAGE OF ORIGINAL)

	Continuous heating in minutes		
	60	120	200
According to bound sulfur	19.5	42.3	41.0
According to bound nitrogen	23.6	31.9	13.1

However, the vulcanization process described may to some degree take place as a result of the reaction of rubber with oxygen molecules or peroxide compounds contained in the original technical products[2]. In order to avoid the complicating action of oxygen, the experiments were confined to purified sodium-butadiene rubber, which was heated in solution in toluene in sealed ampules in a nitrogen atmosphere. A specially compounded mixture containing radioactive sulfur (S^{35}) was used as vulcanizing agent in a number of experiments.

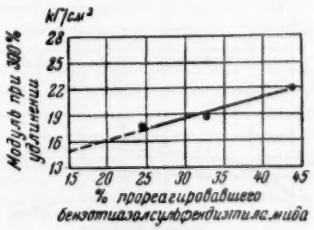


FIG. 2.—Relation of modulus of an unloaded vulcanizate of butadiene-styrene rubber to the amount of benzothiazolesulfendiethylamide reacting. The abscissa represents the *Percentage of benzothiazolesulfendiethylamide* which reacts; the ordinate the *Modulus in kg. per sq. cm. at 300 per cent elongation.*

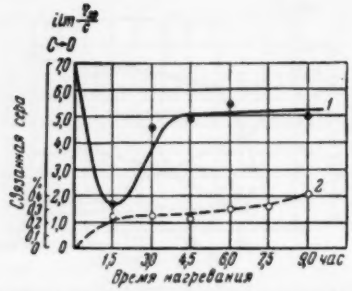
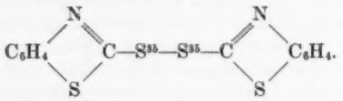


FIG. 3.—Change of viscosity (1) and bound sulfur content (2) during heating of solution of sodium-butadiene rubber with benzothiazolyl disulfide. The abscissa represents the *Time of heating in hours*; the left-hand ordinate the *Bound sulfur in percentage*, and the right-hand ordinate the *Viscosity*.

This compounding procedure assured the presence of radioactive sulfur in the disulfide bridge according to the formula:



The process of vulcanization was followed by the change of viscosity of the solution and the sulfur content of the rubber. At the same time, the decreasing amount of unchanged benzothiazolyl disulfide and the increasing amount of mercaptobenzothiazole were measured. The results obtained are depicted in Figures 3 and 4.

The change of viscosity of the rubber solution (Figure 3) indicates the progress of vulcanization; an initial decrease of viscosity due to grouping of chains inside the molecular aggregate and formation of isolated side-chain molecules. When the individual molecules become united in the spatial network characteristic of a vulcanizate which has attained a final equilibrium modulus, the viscosity increases.

The decrease of the benzothiazolyl disulfide content, combination of its decomposition products with the rubber (determined by the bound nitrogen

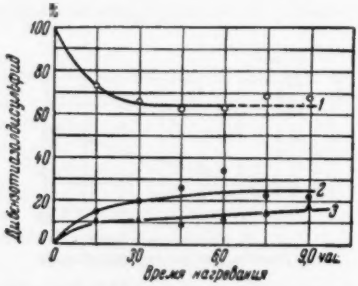
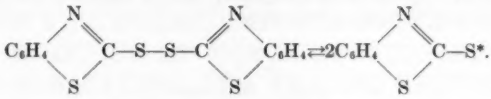


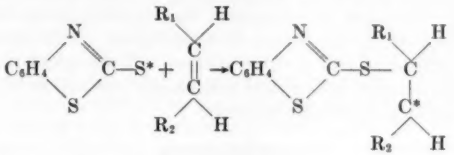
FIG. 4.—Change of benzothiazolyl disulfide (1), mercaptobenzothiazole (2), and sulfur (3) during heating of sodium-butadiene solution (in percentage of original benzothiazolyl disulfide content). The abscissa represents the *Time of heating in hours*; the ordinate the *Percentage of benzothiazolyl disulfide*.

and sulfur), as well as the progressive formation of mercaptobenzothiazole, suggest the following vulcanization mechanism. Decomposition of benzothiazolyl disulfide into radicals takes place according to the scheme:

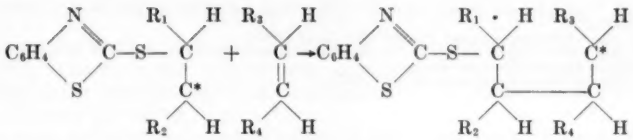


(1)

These radicals either react with the double bonds of the rubber molecules, actuating a polymerization process according to the scheme:

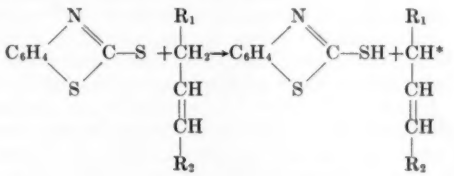


(2)

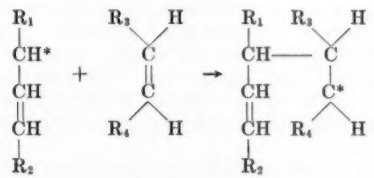


(3)

or else accept the hydrogen α-methylene group of the molecular chains of rubber, and are transformed into a mercaptobenzothiazole molecule, and actuate a polymerization process according to the scheme:



(4)

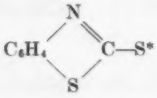


(5)

The latter oxidizing-regenerating vulcanization mechanism is confirmed by the formation of mercaptobenzothiazole, which proceeds parallel to the decrease of benzothiazolyl disulfide content (Figure 4).

In the experiments with radioactive benzothiazolyl disulfide, a radioactive sulfur content was identified in both the vulcanizate and in the acetone extract, with equal intensity of barium sulfate radiation of approximately 100 counts per

min. Such a distribution of intensities can be explained by the decomposition into the radicals indicated in scheme (1) and union of the radicals with the rubber molecules. The vulcanization mechanism of benzothiazolesulfenediethylamide can be represented analogously, proceeding from the possibility of formation from it of radicals of the type:



The phenomenon described, besides being of importance in itself, is interesting from the viewpoint of explaining the mechanism of vulcanization in general and the nature of the action of accelerators. The substances studied are used as accelerators of sulfur vulcanization. It is evident that, in the latter case, an exchange reaction with sulfur takes place[4], as well as the mechanism of radical polymerization investigated above.

REFERENCES

[1] Dogadkin, "Chemistry and Physics of Rubber", 1947; "Studies of the Physics and Chemistry of Rubbers", 1950, p. 21.
[2] Dogadkin and Feldstein, *Kauchuk i Rezina*, No. 12, 12 (1939).
[3] The synthesis was accomplished by M. Ya. Kaplunov under the supervision of E. N. Guryanova in the Karpov Physical-Chemical Institute.
[4] Craig, RUBBER CHEM. & TECHNOL. 24, 262 (1951).

EFFECT OF THE MOLECULAR WEIGHT OF RUBBER ON THE KINETICS OF VULCANIZATION AND ON THE FORMATION OF A SPATIAL NETWORK *

A. S. Novikov, G. M. Bartenev, and F. A. Galil-Ogly

From scientific literature it is known that the rate of vulcanization and the mechanical properties of rubbers depend on the value of the initial molecular weight of the rubber[1]. However, the cause of the slow vulcanization of olw molecular rubbers and the effect of the molecular weight of the rubber on the formation of a spatial network and the structure of the vulcanizate remain unclear. In the present work the kinetics of vulcanization of separate fractions of butadiene rubber SKS-30A of molecular weight from 100,000 to 1,170,000 was studied by measurements of the equilibrium modulus and the proportion of combined sulfur[2]. The SKS-30A rubber was divided into five fractions of molecular weights: I 1,170,000; II 700,000; III 500,000; IV 140,000; and V 100,000. The molecular weights were calculated from viscometric data according to the formula previously established for this rubber by the authors: $[\eta] = 2.96 \times 10^{-4} M^{0.71}$.

In order to keep the molecular weight of the rubber constant, sheets for vulcanization were prepared from a dispersion of the ingredients in a benzene-rubber solution. The composition of the mixture was the same for all the fractions, i.e., 100 parts by weight of rubber, 3 parts of sulfur, 1 part of mercaptobenzothiazole, 5 parts of zinc oxide, 2 parts of stearic acid, and 1 part of phenyl-β-naphthylamine. The sheets were vulcanized in a hydraulic press at 143° C for various periods. The amount of sulfur combined with the rubber was determined by Bolotnikov's method[2], specially adapted to small batches of vulcanizate. The rubber specimens, weighing 0.2–0.3 gram, were extracted in 50 cc. of sodium sulfide, and titrated with 0.01N iodine solution.

Figure 1 shows the relation of the amount of combined sulfur to the time of vulcanization for all the rubber fractions; from this it follows that the rate of combination of sulfur with the rubber does not depend on the molecular weight of the latter. This conclusion is not unexpected, since it is highly improbable that the reactivity of rubberlike diene polymers depends on the value of the molecular weight. Thus, the statement made earlier[3] that low-molecular rubbers vulcanize relatively slowly, is incorrect. Such statements are erroneous because the chemical activity of rubber was not determined according to the rate of combination of sulfur, but according to the change of mechanical properties of vulcanizates.

The relation of the equilibrium modulus to the time of vulcanization, determined by Bartenev's method[4] at 70° C, is shown in Figure 2. For the first rubber fraction, of molecular weight 1,170,000, the modulus is not zero, but is equal to 1.6 kg. per sq. cm. before vulcanization. This indicates the appearance of a spatial network during the drying of the sheet. This can be either the result of possible extension or entangling of the chains[5], which, as a result of the

* Translated for Rubber Chemistry and Technology from *Doklady Akademii Nauk SSSR*, Vol. 94, No. 2, pages 253–356 (1954).

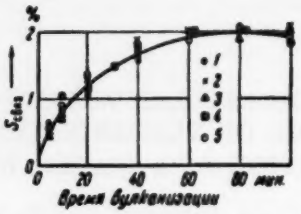


FIG. 1.—Kinetics of combination of sulfur during vulcanization.

1. 1,170,000
2. 700,000
3. 500,000
4. 140,000
5. 100,000

limitation of the number of possible configurations of the network, has an effect similar to that of chemical cross-links, or else is a result of the fact that a partial structure formation may take place at the same time because of oxidation, which is not essential for the low-molecular rubber fractions. The value of the equilibrium modulus for vulcanizates depends on the value of the initial molecular weight of the rubber; with decrease of the molecular weight, there is also a decrease of the equilibrium modulus.

It is noteworthy that the initial moment of formation of a spatial network during vulcanization is determined by the original value of the molecular weight of the rubber and the corresponding proportion of combined sulfur.

The formation of a spatial network in vulcanizates of low-molecular rubber fractions is observed only after a critical time of vulcanization and a critical proportion of combined sulfur. The greater is the initial molecular weight of the rubber, the shorter is the time of vulcanization and the smaller is the quantity of combined sulfur necessary for the initial moment of structure formation in the spatial network. On the basis of the data (Figure 2), it is possible to state that a "critical" value of the molecular weight exists, equal to approxi-

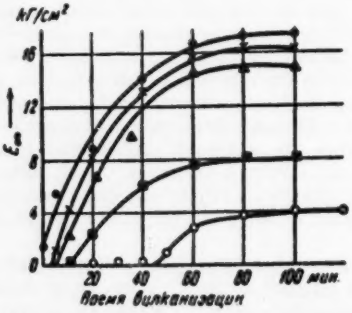


FIG. 2.—Change of equilibrium modulus for vulcanizates of different rubber fractions during vulcanization.

1. 1,170,000
2. 700,000
3. 500,000
4. 140,000
5. 100,000

mately 1,000,000, at which the formation of the spatial network begins at once. This situation fully explains the cause of the so-called "slow" vulcanization of low-molecular rubbers. This phenomenon is caused, not by the change of chemical activity of the rubber with decrease of molecular weight, but by a purely structural factor. Thus, for rapid formation of a spatial network, a definite value of the molecular weight of the rubber is necessary.

The relation between the proportion of combined sulfur necessary for initial formation of a spatial network and the reciprocal of the molecular weight of rubber is expressed graphically by a straight line which passes through the beginning of the coordinates (Figure 3), corresponding to the equation: $S_0 = a/M$, where S_0 is the quantity of sulfur necessary for the initial moment of formation of a spatial network and M is the molecular weight of the rubber.

On the basis of this simple relation, it is possible to determine the value of the molecular weight of rubber by the quantity of sulfur combined up to the initial moment of formation of a spatial network or, for rubber with a known molecular weight, to establish the necessary proportion of sulfur. Experimen-

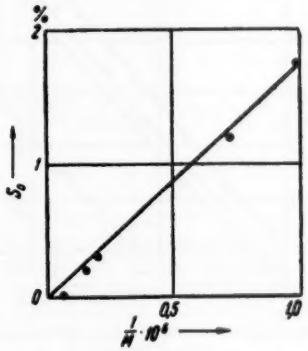


FIG. 3.—Relation between the molecular weight and the proportion of sulfur.

tal verification of this equation showed a quite satisfactory correspondence: if the mean viscosity molecular weight of unfractionated rubber SKS-30A was 326,000, the molecular weight measured from the quantity of combined sulfur before the beginning of formation of a spatial network was equal to 295,000. Thus, the existence of a critical value of the molecular weight, 1,000,000, showed that during vulcanization of rubber with a molecular weight below 1,000,000, there is at first a cross-linking into larger formations, involving the sulfur in the separate molecular chains. Only when the molecular chains reach a definite size does the subsequent combination of sulfur lead to the formation of a continuous spatial network in the vulcanizate. It is natural to suppose that the sulfur consumed in enlarging the molecular chains does not take part in the formation of cross-links in the final stage of vulcanization. If the index of the number of unions in a vulcanizate is calculated by Bartenev's formula[6]: $E_\infty = CN^{\frac{1}{3}}$ or $[N] = E_\infty^{\frac{1}{3}}$ (where E_∞ is the equilibrium modulus in kg. per sq. cm., C is a constant for the given type of rubber and $[N]$ is the number of chains in a unit volume) and the change in relation to the amount of sulfur entering the formation of a network during vulcanization is followed, then linear relations

between the number of unions (N) and the amount of combined sulfur S are obtained for all the rubber fractions (Figure 4). The identical slopes of all the curves in Figure 4 show that the rate of formation of a network in the vulcanizate after a definite amount of sulfur has combined for each rubber fraction does not depend on the initial value of the molecular weight of the rubber.

Determining with a certain accuracy the quantity of sulfur entering only into the formation of chemical cross-links, it becomes possible to calculate the number of sulfur atoms necessary to form one union. Utilizing the linear relation between the index of number of unions and the quantity of sulfur [S_1] entering into the formation of the spatial network, it is possible to determine by extrapolation the value of the equilibrium modulus and the amount of combined sulfur at the early stages of vulcanization near the initial moment of formation of the spatial network. The experimental measurement of these

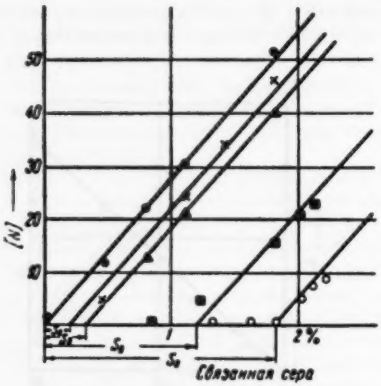


FIG. 4.—Relation between the index number of unions and the proportion of combined sulfur.

1. 1,170,000
2. 700,000
3. 500,000
4. 140,000
5. 100,000

quantities is complicated and unreliable because of the insufficient sensitivity of the methods used. At the same time, on the basis of these data, it is possible to characterize reliably the structure of the vulcanizate and the type of sulfur bonds formed. In Table 1, calculations of the number of sulfur atoms per union for vulcanizates of all the SKS-30A fractions are given, (E_∞) and the amount of sulfur combined during the initial stages of vulcanization were measured by extrapolation of the curves in Figure 4 on the abscissa. The number of cross-links in the vulcanizate was calculated[7] by the approximate relation: $E_\infty = 3\,NKT$. The number of unions was assumed to be equal to one-half the number of chains in a unit volume.

In the early stages of vulcanization, approximately two atoms of sulfur are necessary for each union. Consequently, in the presence of mercaptobenzothiazole, disulfide bonds are formed in the first stage of vulcanization. As vulcanization continues, the number of sulfur atoms remains constant and equal, on the average, to about two per union for vulcanizates of all the rubber fractions.

This is confirmed by the constant relation of the index of the number of unions to the quantity of combined sulfur, $[N]/S_1$. In the early stage of vulcanization, this relation was 29.6 for vulcanizates of all the rubber fractions, and at the moment of completion of the network (at the optimum state of vulcanization) it was 34.4 for fraction I, 35.4 for II, 34.8 for III, 29.5 for IV, and 28 for V, which must be considered practically the same.

However, the constant average value of the number of sulfur atoms per union does not exclude the possibility that, along with the disulfide bonds in the vulcanizate, there are also, at optimal vulcanization time, monosulfide and polysulfide bonds, formed as a result of primary reactions of the rubber with the sulfur and accelerator, and also as a result of the redistribution of the sulfur

TABLE 1*

Molecular weight of the rubber	Total amount of bound sulfur in %	Amount of sulfur necessary for initial moment of formation of spatial network S_0 in %
1,170,000	0.04	—
700,000	0.22	9.18
500,000	0.35	0.31
140,000	1.24	1.2
100,000	1.84	1.8

* For the formation of transverse bonds, the sulfur $S = 0.04\%$; $E_{sp} = 1.13$ kg. per sq. cm.; the number of chains in 1 cc. $N = 8 \times 10$; the number of unions in 1 cc., $n = 4 \times 10^{19}$; number of sulfur atoms per union, 2.

bonds and reaction of free sulfur with combined sulfur during prolonged vulcanization.

Vulcanizates of low-molecular rubber differ in structure from those of high-molecular rubber; in the first case the sulfur which first combines with the rubber enters directly into the segments of the molecular chains between the unions of the network. This fact may influence the nature of the inter-molecular reaction and, accordingly, the relaxation and mechanical properties of vulcanizates.

REFERENCES

[1] Vanko, *J. Polymer Sci.* **4**, 576 (1948); Penn, *India-Rubber J.* **69**, No. 4, 4 (1950); Novikov, Khaikina, et al., *Kolloid. Zhur.* **15**, 51 (1953).
[2] Bolotnikov and Gurova, *Zhur. Rezina Prom.* **10**, No. 6, 61 (1953).
[3] Vanko, *J. Polymer Sci.* **4**, 576 (1948).
[4] Bartenev, *Zhur. Tek. Fiz.* **22**, No. 7, 1154 (1952).
[5] Flory, *Ind. Eng. Chem.*, **38**, 417 (1946).
[6] Bartenev and Vishnitskaya, *Zhur. Tek. Fiz.* **20**, 858 (1950).

DEPENDENCE OF THE FUNDAMENTAL PROPERTIES OF UNVULCANIZED AND VULCANIZED BUTADIENE-STYRENE RUBBER MIXTURES ON THE INITIAL MOLECULAR WEIGHT *

A. S. Novikov, M. B. Khaikina, T. V. Dorokhina, and M. I. Arkhangelskaya

Scientific Research Institute of the Rubber Industry, Moscow, USSR

Recently a number of works have been devoted to the study of the relation of the mechanical properties of raw polymers[1] and vulcanized polymers to their molecular weight[2]. In the present paper, an attempt is made to determine the basic properties of unvulcanized and vulcanized SKS-30A rubber-carbon black mixtures as functions of the initial molecular weight, with the purpose of establishing the limits of molecular weight for the complete retention of the technical properties of the vulcanizates. In addition, the effect on the properties of raw mixtures and vulcanizates of the addition of a low-molecular fraction to the high-molecular fraction was determined. SKS-30A rubber was chosen for this study because it is completely soluble in benzene, and also because it posseses the best technical properties of the butadiene-styrene rubbers in industrial use at the present time.

EXPERIMENTAL METHOD

Fractionation.—The rubber was separated into fractions at 25° ± 0.05° C from a 1 per cent benzene solution (free of thiophene) by the fractional precipitation method worked out by Flory[3] and perfected by Zhukov, Puddubnyi, and Lebedev[4]. Methanol was used as precipitant. One hundred and twenty grams of rubber was divided into five fractions. In order to exclude completely the action of oxygen, the fractions were dried in vacuo at 20–25° C, repeatedly treated with nitrogen from which oxygen had been eliminated, and then 1 per cent of phenyl-β-naphthylamine was added. However, despite the precautions taken, it was impossible to prevent structure formation during the drying of the highest molecular fraction. The relative viscosities of the fractional solutions in benzene were measured in an Ostwald viscometer for volatile liquids at 25° ± 0.05° C.

The molecular weight of each fraction was calculated from the equation: $[\eta] = 2.96 \times 10^{-4} M^{0.71}$, derived previously for this rubber from the established linear relation of the logarithm of the limiting viscosity for the separate fractions to the logarithm of the molecular weight of the same fractions, determined osmotically in an apparatus constructed by Zhukov, Poddubnyi and Lebedev[5]. The values of the molecular weights and the amounts of the fractions isolated are shown in Table 1.

Preparation of the mixtures and their vulcanization and testing.—The mixtures for fractionation and the unfractionated rubber were prepared from the following recipe:

* Translated for Rubber Chemistry and Technology from the *Kolloidnyi Zhurnal*, Vol. 15, No. 1, pages 51–59 (1953).

	Parts by weight
Rubber	100
Channel carbon black	50
Rubberax	5
Zinc oxide	5
Stearic acid	2
Sulfur	2
Mercaptobenzothiazole	2

The rubber was mixed with the other ingredients on a micromill of 35 × 160 size with the friction ratio, 1:1.2, and roll temperature 20–30° C. The mixture was prepared from 7 grams of rubber. The ingredients were weighed on an analytical balance. The order of addition of the ingredients and the mixing time were the following. The rubber was mixed with Rubberax for three minutes; in the next three minutes the mercaptobenzothiazole and stearic acid were added, then equal parts of zinc oxide and carbon black were added in four portions, each during three minutes, with a total mixing time of 26 minutes. Before vulcanization, the mixtures were let stand for 24 hours, and then samples to be vulcanized were sheeted on a calender in the form of films 0.3–0.4 mm. thick. For the stiff mixtures of the first and second fractions, the raw mixtures were also pressed at 60–70° C for 10–20 minutes, in order to obtain the necessary thickness.

Vulcanization was carried out in a special mold, with chromium-plated internal surfaces, in a hydraulic press at 143° C for 60, 90, 100, and 120 minutes. The most important feature of the construction of the mold was a shock absorber of vulcanized rubber to overcome the irregularities of the sheets and mold and to obtain vulcanized films $\sim 0.3 \pm 0.05$ mm. thick.

The vulcanized sheets of 90 × 110 mm. were cut into strips 25 mm. wide and 90 mm. long, from which strips 3.25 × 25 mm. were cut. It was thus possible to obtain about 100 test-specimens from one vulcanized sheet weighing 1.2–1.3 grams; this made possible several tests with a limited quantity of rubber. This represents an essential advantage of the method over that described in the literature[6].

The basic physical and mechanical indexes of the vulcanizates: equilibrium modulus determined by the method of Bartenev[7], tensile strength, relative elongation and heat resistance at 95° C were determined on a Mendele dynamometer with the lower clamp moving at the rate of 10 mm. per minute.

The average value of each index was derived from seven or eight experiments.

TABLE 1

MOLECULAR WEIGHTS AND AMOUNT OF FRACTIONS ISOLATED

Number of fraction	$[\eta]$	tan of angle of inclination of the curve $\left(\frac{\eta_{sd.}}{c} \text{ to } c\right)$	Molecular Weight $[M]$	Amount (grams)	Amount (%)
1*	—	—	>1,000,000	26.6	22.9
2	5.20	4.5	951,500	24.2	20.8
3	2.20	4.0	283,300	25.2	21.7
4	1.50	0.62	165,200	24.3	20.9
5	0.90	—	80,500	16.0	13.7
Non-fractionated	3.6	5.0	M_n 197,000 M_v 562,300	—	—

* $[\eta]$ and M of the first fraction could not be measured, because this particular fraction was not soluble in benzene.

The resistance to repeated deformations was determined on a Gul[8] apparatus with initial amplitude of 150 per cent and constant final deformation load.

The carbon black-rubber gel in the unvulcanized mixtures and the swelling index were determined as follows. A finely cut batch of carbon-black mixture weighing about 2 grams was immersed in benzene for 40 hours at 25° C. After swelling, the specimen was weighed, dried to constant weight, and the amount of carbon black bound with the rubber was determined.

The calculation was made according to the formula:

$$\text{Rubber bound with carbon black (\%)} = \frac{\text{(Weight of dry gel minus weight of carbon black in gel)} \times 100}{\text{weight of rubber in batch}}$$

$$\text{Swelling index} = \frac{\text{(weight of swollen gel minus weight of dry gel)} \times 100}{\text{weight of dry gel}}$$

The thermoelastic properties of the unvulcanized mixtures were determined on a Kargin scale by measuring the degree of deformation of specimens of 6 × 5 mm. size in the temperature range of 19° to 150° C. The initial degree of deformation for all the specimens was equal to 5–6 per cent for the load chosen.

PROPERTIES OF UNVULCANIZED MIXTURES

The fractions isolated differed in appearance and in behavior on a mill. The first fraction was a stiff elastic product. At the beginning of milling, this fraction was difficult to break down, gave no film, and did not adhere to the rolls. The second fraction was softer and had less nerve in comparison with the first. The third fraction resembled unfractionated rubber in appearance and behavior on the rolls. The fifth fraction was viscous and sticky at room temperature and smeared on the surface of the rolls, but, with the addition of the first portions of carbon black, it formed a film. The fourth fraction occupied an intermediary position between the third and fifth, approximating more closely, however, the third fraction.

The initial portions of carbon black were more difficult to add to the first fractions. However, the carbon black could be dispersed better in the high-molecular fractions than in the low-molecular ones; this is illustrated by the microphotographs of the unvulcanized mixtures (Figure 1). This confirms the hypothesis, well known in the technology of the preparation of mixtures, that the best dispersion is obtained with initial addition of a hard type of material to the rubber; for example, during mixing, relatively hard materials (e.g., channel carbon black) should be added to the rubber first, and then the remaining ingredients and plasticizing agents.

In the mixing of rubber with channel carbon black, an insoluble carbon-rubber complex is formed, with transformation of part of the dissolved rubber into the insoluble state. In mill-mixing of fractions with carbon black, it was established that the binding of rubber with carbon black increases sharply with an increase of the initial molecular weight up to 300,000, and then remains constant with further increase of molecular weight.

The structure of the insoluble carbon black-rubber complex formed is different for the separate fractions; the densest structure of the gel for relatively small swelling values is observed in mixtures of fractions with $M \sim 300{,}000$ and higher; with a decrease of M, the swelling values of the gel increase, with a simultaneous decrease of the quantity of bound rubber, indicating a looser

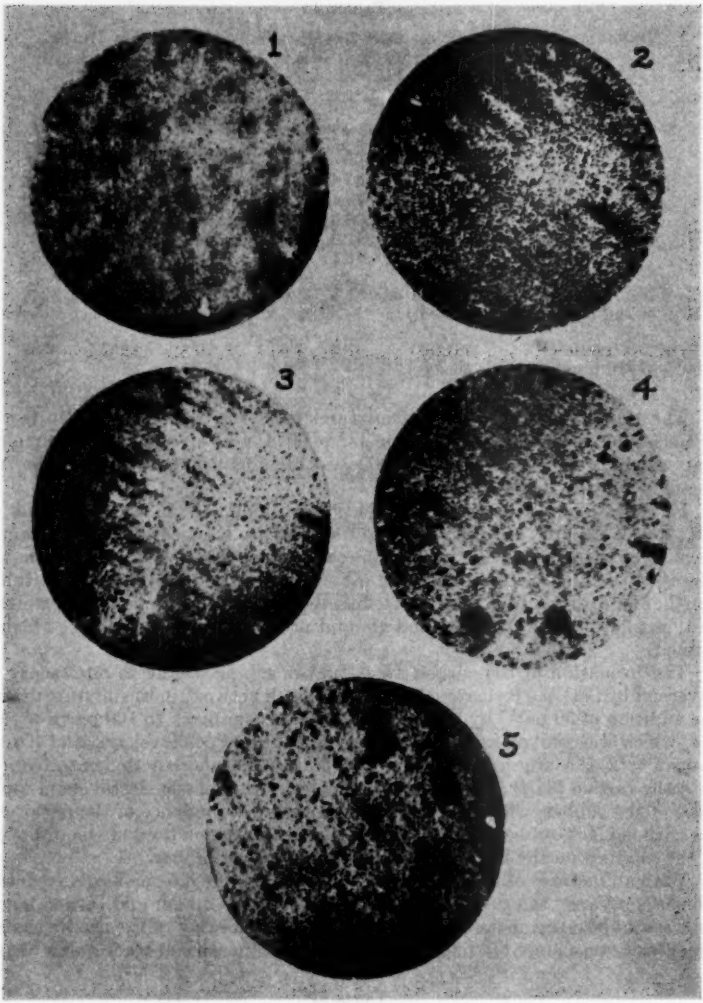


FIG. 1.—Photomicrographs of unvulcanized mixtures of five fractions.

1 First fraction
2 Second fraction
3 Third fraction
4 Fourth fraction
5 Fifth fraction

structure of the carbon-rubber gel. Addition of a low-molecular fraction to the high-molecular one sharply decreases the amount of rubber bound with the carbon black, and increases the swelling values of the gels. Thus, these properties of rubber-carbon black mixtures are a function of the mean molecular weight of the rubber.

TABLE 2

BEHAVIOR OF FRACTION OF SKS-30A RUBBER WITH CARBON BLACK IN STANDARD MIXTURE

No. of fraction	Molecular weight (M)	Amount of gel (%)	Carbon black content in gel (%)	Quantity of rubber bound with carbon black (%)	Value of swelling in calculation for	
					gel	rubber
1	1,000,000	69.8	47.3	61.5	1227	1995
2	951,500	73.4	46.9	64.7	1230	1902
3	283,300	68.5	44.5	63.8	1013	1588
4	165,200	51.0	61.2	31.3	1158	3700
5	80,500	41.1	73.3	18.2	1053	5786
50% of 5th fraction 50% of 2nd fraction	516,000 (calcd.)	51.8	60.1	37.4	1213	3244
50% of 5th fraction 50% of 3rd fraction	181,900 (calcd.)	47.6	63.1	29.1	1262	4337

The transition temperature of mixtures from the high-elastic state to the viscous-fluid state, T_f, increases from 44° to 80° C with an increase of the molecular weight from 80,000 to ~300,000 and remains constant with further increase of M (see Table 3).

If we assume that the above-mentioned differences in the properties of mixtures of the first, second, and third fractions are reduced to a certain degree because of the equalization of the molecular weights which takes place in the process of mixing on rolls[9], then the differences in the properties of the third, fourth, and fifth fractions can be attributed only to the mean molecular weight, and, possibly, to the structure and amount of carbon black-rubber gel which is formed.

The formation of the carbon black-rubber gel, according to our theory, is governed by: (1) the formation of a carbon black network in the mixture during the addition of 50 parts by weight of channel carbon black to 100 parts of rubbre, which was proved in experiments of Dogadkin, Pechkovskaya, and Kupriyanova[10]; (2) the large amount of energy of intermolecular reaction of the rubber with the carbon black and the degree of interlocking of the elastic chain molecules of the rubber, which follows the established dependence of the density of the carbon black-rubber gel, determined by the swelling index and amount of gel in the mixture on the initial molecular weight of the rubber.

With an increase of the initial molecular weight, the intermolecular reaction increases between the rubber chains and between the rubber and carbon black, with a simultaneous increase of the degree of interlocking of the elastic chains, which will cause more binding of the rubber with the carbon black and a denser

TABLE 3

RELATION OF THE T_f VALUE OF CARBON BLACK MIXTURES OF RAW SKS-30A TO THE ORIGINAL MOLECULAR WEIGHT OF RUBBER

No. of fraction	Molecular weight (M)	T_f (° C)
1	1,000,000	82
2	951,500	82
3	283,300	80
4	165,200	62–66
5	80,500	44

TABLE 4

RELATION OF PHYSICAL-MECHANICAL PROPERTIES OF VULCANIZATES TO INITIAL MOLECULAR WEIGHT

No. of fraction	Initial molecular weight M	Optimum vulcanization time (minutes)	Amount of rubber bound with carbon black (%)	Equilibrium modulus (kg. per sq. cm.)	Tensile strength (kg. per sq. cm. at 20° C)		Tensile strength (kg. per sq. cm. at 95° C)		Relative elongation (% at 20° C)	Relative elongation (% at 95° C)	Coefficient of heat resistance at 95° C		Number of cycles before destruction of specimens
					On original cross-section	On actual cross-section	On original cross-section	On actual cross-section			Based on tensile strength	Based on relative elongation	
1	>1,000,000	80	61.5	36	274	3241	71	324	1121	355	0.26	0.32	6680
2	951,500	80	64.7	23	250	3001	75	372	1062	387	0.30	0.36	6800
3	283,300	80	63.8	25	241	2490	68	318	927	352	0.28	0.38	6230
4	165,200	80	31.3	18.9	226	1688	57	200	645	374	0.25	0.58	5660
5	80,500	120	18.2	8.8	124	868	27	108	595	305	0.22	0.51	1981
5 + 2 (1:1)	516,000 (calcd.)	100	37.4	19.9	159	986	25	78.5	525	216	0.157	0.412	1755
Unfractionated	197,000	80	27.0	—	205	1640	60	309	707	411	0.292	0.581	—

structure in the carbon-rubber gel. One should not exclude the possible formation of strong rubber-carbon black chemical bonds, formed either as a result of reaction with the carbon black of groups formed in the rubber during oxidation, or as a result of the initial reactions of the double bonds of the rubber with the carbon black, with participation of oxygen. The latter is confirmed by the insolubility of the carbon-rubber gel even after heating in a boiling solvent.

PROPERTIES OF THE VULCANIZATES

It was most interesting to investigate the change of the fundamental properties of vulcanizates in relation to the initial molecular weight of the rubber. All the fractions were tested in a single recipe, i.e., with identical proportions of vulcanizing and accelerating agents, and with testing conditions comparable to those used in determining the properties of technical rubber mixtures.

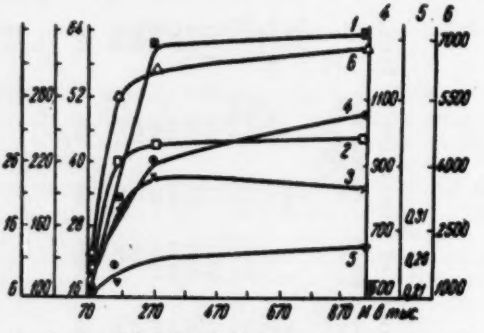


FIG. 2.—Relation of physical-mechanical properties to molecular weight

1 Quantity of rubber bound with carbon black.
2 Tensile strength in kg. per sq. cm.
3 Equilibrium modulus, E_∞, in kg. per sq. cm.
4 Elongation in percentage.
5 Coefficient of heat resistance based on tensile strength.
6 Number of cycles before destruction of specimens.

First, three different proportions of accelerator and sulfur, viz., 1.2, 1.5, and 2 parts of weight of each, in 100 parts of rubber were tested. The best indexes were obtained for mixtures of all fractions with 2 parts of accelerator and sulfur; all the tests were made with this recipe. The combined sulfur contents in the vulcanizates for all the fractions averaged the same (1.72 parts by weight); this may indicate an equal number of cross-links.

Table 4 and Figure 2 show the change of the equilibrium modulus, tensile strength, relative elongation, coefficient of heat resistance, and fatigue resistance during stretching of vulcanizates of the five isolated fractions, compared with the properties of the vulcanizate of unfractionated rubber and a vulcanizate of the combined fractions.

The equilibrium modulus and tensile strength increase with increase of the original molecular weight of the fractions, and the greatest increase is observed at a molecular weight of ~300,000. At higher values of the molecular weight, the increases of tensile strength and equilibrium modulus do not take place or these changes are quite small. In this particular case, the phenomenon of equalization of the molecular weight for the first, second, and third fractions in

the mixing process is again observed. The tensile strengths of vulcanizates of the first four fractions (274–226 kg. per sq. cm.) are higher than for the unfractionated rubber (205 kg. per sq. cm.); for the fifth fraction the tensile strength is much lower (124 kg. per sq. cm.)[11].

The relative elongation increases right up to M = 1,000,000; however, the greatest value is in the range up to 300,000.

In the combining of a fraction with high M (2nd fraction) with a low-molecular fraction (5th fraction) in the proportion 1:1, large decreases of tensile strength and relative elongation are observed, even when the high mean value of M is retained. Thus, at the given extreme value of M, there is no additivity in the change of the basic mechanical properties of vulcanizates.

The coefficient of heat resistance, based on tensile strength, which characterizes the retention of the latter at 95° C, is somewhat reduced, viz., from 0.30 to 0.22, with a decrease of initial M. The absolute value of the tensile strength at 95° C, calculated from both the initial cross-section of the specimen and the

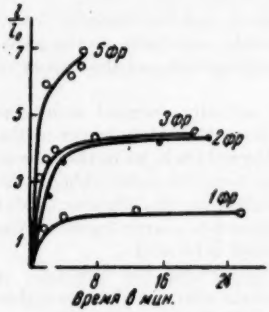


FIG. 3.—Development of dynamic relaxation by the process of repeated deformations. The abscissa represents the *Time in minutes*. The curves numbered *1*, *2*, *3*, and *5* are the *Fraction numbers*.

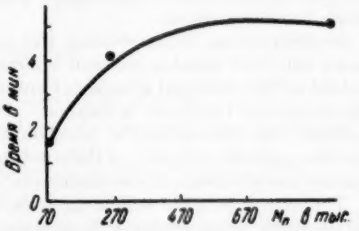


FIG. 4.—Relation of rate of relaxation to molecular weight. The ordinate represents the *Time in minutes*.

real section, remains dependent on the initial M value, analogous to the relation established during testing at 20° C. The coefficient of heat stability, based on relative elongation, increases with decrease of initial M from 0.32 to 0.51. This may be explained by the partial development of plastic flow.

The fatigue resistance during repeated deformations with constant final deforming load (see Figure 2, curve 6) increases greatly with increase of the mean molecular weight of the rubber; with increase of M from 80,000 to 300,000, the number of cycles before destruction of the specimen increases from 1981 to 6230, that is, there is an almost direct relation between the value of M and the capacity of the vulcanizate to resist repeated deformations.

In the combination of fractions with extreme values of M, a sharp decrease of resistance to repeated deformation is observed, just as in the case of change of tensile strength, despite the preservation of very high mean values of the molecular weight. In the process of repeated deformations the specimens are gradually stretched. Karmin and Epstein proposed to call this phenomenon the dynamic relaxation.

Figure 3 shows that curves of development of dynamic relaxation for vulcanizates of different fractions. If the curvilinear segment is regarded as the

region which characterizes the passage of the system to mechanical equilibrium, then the time interval necessary to effect this, called in the work of Gul, Dorokhina, and Dogadkin[8] the rate of relaxation, can give the relative mobility of the chain molecules. Figure 4 shows the rate of relaxation as a function of M. This figure shows that the chains of the vulcanizates of the low-molecular fractions possess the highest rates of relaxation and, consequently, relatively great mobility.

The dependence of the basic properties of vulcanizates on the initial molecular weight of a rubber can be explained by the more regular structure of the spatial network in high-molecular fractions in comparison with low-molecular fractions, and by the nature of the reaction of these fractions with carbon black. In the case of an equal number of cross-links, the number of free terminal groups not entering into the chain will be much greater in vulcanizates of low-molecular fractions; this was shown by Flory[12] for Butyl rubber. The possibility is not excluded that, for low-molecular fractions, the chain can be ruptured, as is evident in the development of plastic flow.

According to the theories developed by Dogadkin, and Sandomirskii[13], and Lukin and Kasatochkin[14], the tensile strength depends principally on the partially oriented molecular chains up to the moment of rupture and the energy of intermolecular reaction.

In deformation by stretching, the number of partially oriented molecular chains and their number per unit volume will be proportionately larger as the content of free terminal groups not entering into the network, as in the case of high-molecular fractions, is smaller. At the same time, in carbon-black vulcanizates, the intermolecular reaction will be greatest for the high-molecular fractions, and the intensity of the reaction is determined to a large degree by the amount and structure of the carbon-rubber gel which is formed.

The characteristics which have been noted concerning the structure of carbon-black vulcanizates of high-molecular fractions also explain the higher tensile strength and resistance to repeated deformations.

The rate of growth of the primary nucleus of destruction which forms during fatigue, and probably its origin as well, will be less the greater the degree of orientation of the molecular chains and the total energy of intermolecular reaction. From this it follows that the destruction of rubber during fatigue is governed, not only by the course of the oxidation processes, but also by the structure of the vulcanizate. From this viewpoint, the application of the principle of synthesis of high-molecular rubbers with a view to increasing fatigue resistance seems expedient.

CONCLUSIONS

1. The relation of the basic properties of unvulcanized and vulcanized SKS-30A rubber-carbon black mixtures to the initial molecular weight of the rubber was studied.

2. Fractions having molecular weights up to 300,000 possess the best technical properties in their behavior during mill mixing. However, the best dispersion of carbon black is found in the still higher molecular fractions.

3. In the mill mixing of rubber with carbon black, it is principally the highest molecular fractions of the rubber which become bound, with the formation of an insoluble carbon black-rubber gel. It is shown that the thermoplastic properties of rubber-carbon black mixtures depend basically on the molecular weight and, probably, on the structure and quantity of carbon black-rubber gel formed.

4. The basic properties of vulcanizates, viz., tensile strength, relative elongation, heat resistance, and resistance to repeated deformations increase with increase of the molecular weight up to 300,000, but change little with further increase of the molecular weight.

5. The greatest reduction of the properties of vulcanizates is observed at a molecular weight of 80,000 and lower. Addition of a low-molecular fraction to a high-molecular fraction in the proportion of 1 : 1 greatly decreases the tensile strength and resistance to repeated deformation.

6. The range of molecular weights from 100,000 to 300,000 is, for SKS-30A rubber, the most satisfactory from the viewpoint of obtaining, throughout this range, satisfactory technical properties of mixtures before vulcanization and physical and mechanical properties after vulcanization.

7. The relation which has been established of the basic properties of a vulcanizate to its molecular weight is explained: (1) by the formation of a more regularly constructed network in a vulcanizate of the high-molecular fractions of rubber, which is distinguished from that of the low-molecular fractions by a smaller number of terminal groups not entering into the chain; and (2) by the different nature of the reaction between carbon black and the high-molecular fractions, resulting in the latter case in a higher value of the energy of intermolecular reaction.

REFERENCES

[1] Zapp and Baldwin, *Ind. Eng. Chem.* **38**, 948 (1946).
[2] Janke, *J. Polymer Sci.* **3**, 586 (1945); Johnson, *Ind. Eng. Chem.* **40**, 351 (1948).
[3] Flory, *J. Chem. Physics* **11**, 521 (1943).
[4] Zhukov, Poddubnyi, and Lebedev, "Studies of High-Molecular Compounds", Acad.Sci.USSR, **1949**, p. 238.
[5] Zhukov, Poddubnyi, and Lebedev, *Kolloid. Zhur.* **10**, 423 (1948).
[6] Flory, *Ind. Eng. Chem.* **38**, 418 (1946); Juve and Schroeder, *Ind. Rubber World* **115**, 4 (1947).
[7] Bartenev, *Kolloid. Zhur.* **11**, 57 (1949); Since with carbon-black vulcanizates a state of equilibrium is not attained, the modulus is called the conventional modulus.
[8] Gul, Dorokhina, and Dogadkin, *Kolloid. Zhur.* **13**, 339 (1951).
[9] Novikov and Koloskova, *J. Chem. Ind.*, No. 12, 353 (1951); We established for SKS-30A rubber that, during mechanical plasticization, an equalization of the molecular weights takes place as a result of destruction, chiefly, of the high-molecular fractions.
[10] Dogadkin, Pechkovskaya, and Kupriyanova, "Studies of the Physics and Chemistry of Raw and Vulcanized Rubber", Gov. Chem. Press, **1950**, p. 103.
[11] The somewhat reduced absolute tensile-strength values are the result of having carried out the test at a low rate of deformation: 10 mm. per minute instead of that standard for rubbers, viz., 500 mm. per minute.
[12] Flory, *Ind. Eng. Chem.* **38**, 417 (1946).
[13] Dogadkin and Sandomirskii, *Kolloid. Zhur.* **13**, 267 (1950).
[14] Lukin and Kasatochkin, "Studies of the Physics and Chemistry of Raw and Vulcanized Rubber", Gov. Chem. Press, **1950**, p. 74; Lukin, *Zhur. Tech. Fiz.* **21**, 663 (1951).

ELECTRIC MEASUREMENTS OF RUBBER–CARBON BLACK SYSTEMS *

GOTTHOLD KICKSTEIN

LABORATORY OF THE METZELER GUMMIWERKE A.G., MUNICH, GERMANY

INTRODUCTION

The addition of active carbon black to rubber causes considerable reinforcement and, hence, improves the serviceability of rubber products. On the other hand, electrically conductive carbon black imparts to rubber-carbon black mixtures a strongly polar character which is reflected in the electric constants[1].

The specific direct current-resistance is frequently changed by several decimal powers by the addition of carbon black. With very small concentrations of carbon black, the resistance at first increases somewhat, probably as a result of union of ions by the carbon black.

With somewhat greater concentrations (over 10–15 per cent by weight), the resistance decreases slowly, and at 30–35 per cent by weight it reaches a maximum, beyond which it suddenly decreases sharply and, with increasing concentrations (about 70 per cent by weight), approaches a saturation value almost asymptotically. This trend was proved to be true of the system: natural rubber-CK-IV carbon black. Here it must be noted that the exact course of the curve is of only slight significance, since the values obtained are decisively influenced by the nature and duration of the mixing process, the time and temperature of storage, preliminary treatment, temperature of measuring, field strength, and form and quality of electrode, and especially by the duration of the measurements[2]. The direction of the influence of these variables is quite interesting.

Mixing on a roll mill gives in most cases higher specific resistance than does mixing in an internal mixer. If samples are taken after so mixing, but before the product is put on a roll mill, no significant difference in the resistance of individual batches is observed, even if they are mixed at different temperatures.

This situation is different if the masticated product is then milled for about 5 minutes before the samples are taken. In order to explain these conditions more clearly, a representative measurement may be cited. This mixture was

Smoked sheet	100 parts by weight
Carbon black (CK-IV)	50 parts by weight

milled for 15 minutes in a GK-5 machine, at 35 rev. per min. of the masticator blade. Milling was carried out immediately after mixing on a 1-liter laboratory mill with 5 mm. distance between rolls.

In the last column an increase of specific resistance with temperature of mixing is observed; at high mixing temperatures, however, the final value of the specific resistance again decreases. The differences are at any rate not very striking.

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from *Kautschuk und Gummi*, Vol. 7, No. 3, pages WT 50–55, March 1954. This paper was presented at a meeting of the German Rubber Society in Goslar, May 7–9, 1953.

The influence of the time of milling is consistent; the specific resistance first rises very rapidly, then more and more slowly to a constant value. If milling is continued too long, a further increase is observed, which, under certain conditions, reaches the same value as that of unloaded rubber.

After each mechanical working, a stiffening of the carbon black batch is observed during storage. At the same time, the specific resistance decreases. This process is accelerated by elevated temperatures.

The measured resistance value of a batch depends on the field intensity used in the measurement; that is, at relatively high field intensities, a smaller resistance is observed.

It is surprising in this connection that the smaller resistance appears instantaneously at higher field intensities, i.e., if, for example, instantaneous values are plotted against voltage with alternating current of 50 cycles per second, a more or less sharply curved cubic parabola is obtained, depending on the form of the electrode. Its curvature is a measure of the nonlinearity (field intensity relation) of the resistance. Besides this inertialess and completely reversible field intensity relation, there is yet another, which gives a smaller resistance when the influence of the field intensity lasts longer. This process is due to electrostatic flocculation of the carbon black particles. (These phenomena have been most thoroughly studied for graphite suspensions[3].)

TABLE 1

	Number of batches studied	Maximum mixing temperature (° C)	Specific resistance of unmilled batch in Ω per cm.	Specific resistance after milling 5 min. in Ω per cm.
Masticator	2	83–92°	3.4×10^{7}–1.3×10^{8}	1.2–3.2×10^{10}
Masticator	4	128–137°	2.1–7.9×10^{7}	1.8–5.4×10^{11}
Masticator	3	169–184°	2.8–8.6×10^{7}	4.3–7.6×10^{10}
Mill	4	ca. 75°	2.3–5.8×10^{9}	8.7×10^{9}–2.8×10^{10}

Like the resistance of rubber-carbon black systems, the dielectric constant varies greatly and depends in a decisive way on the conditions of processing and measurement. In general, the dielectric constant varies in the same way that the conductivity does. This is not always the case, however. Furthermore, the dielectric constant of rubber-carbon black systems depends to a high degree on the temperature. At very high frequencies it has a relatively low value, but then, at frequencies of about 10 cycles per second and lower, it rises slowly at first, and then more rapidly. It steadily increases toward zero frequency, and values of several hundred can be obtained for the dielectric constant if a sufficiently low test frequency is chosen.

The dependence of the dielectric constant on the carbon-black concentration is analogous to the direct-current conductivity. However, no fall of the dielectric constant below the value for nonloaded rubber is observed at very small concentrations; but it increases as an approximately linear function of the carbon black concentration. At concentrations of about 5 per cent by weight of carbon black, however, the dielectric constant diverges from this linear increase and increases even more sharply. Thus, in a range in which the conductivity even decreases compared with unloaded crude rubber, the dielectric constant increases noticeably. It also manifests the sudden change already mentioned in the discussion of resistance. This abrupt change, according to our observations, appears somewhat earlier than the corresponding change of resistance. These general facts are also true of the natural rubber-carbon black (CK-IV)

system. Here the exact course of the curve of the dielectric constant as a function of concentration is of less significance, for it can hardly be reproduced within tolerable limits of error. Again it is the influential factors which interest us[4].

The dielectric constants of milled mixtures are in most cases lower than those of masticated mixtures prepared at various temperatures; in addition, the constant of masticated mixtures increases quite sharply for temperatures over 160° C. The influence of the mixing time is just what would be expected from the conductivity measurements. With increasing time of milling, the constant decreases rapidly at first, then more slowly, while the resistance increases to the same degree. During storage, a decrease of the constant is often observed, although in some cases there is an increase. The temperature of measurement can have a decisive influence on this constant. If a cold sample is heated and the measurements are made a little later, both increase of resistance and decrease of dielectric constant are observed. If the sample is conditioned for a long time at an elevated temperature, the constant again increases as a result of flocculation of the carbon black particles.

The dielectric loss angle of rubber-carbon black systems changes as a function of frequency much as does the dielectric constant, i.e., it decreases at high frequencies and increases sharply toward zero frequency.

The dipole theory of Debye[5] as well as the theory of Wagner[6] require a maximum dielectric loss at a definite frequency. This maximum is displaced by heat effects. Although the loss level may have large values in a rubber-carbon black system, such a maximum can not be established. The experimental results are, at any rate, not conclusive in this respect, so measurements at very low frequencies were necessary. In addition, an attempt was made to displace the maximum by changing the temperature in order to find a suitable range for the measurements. This was not successful, however. Measurements of the loss angle of rubber-carbon black systems in the low-frequency ranges are quite difficult, and, in bridge methods, no definite minimum is reached.

OTHER ELECTRICAL METHODS OF MEASUREMENT AND THEIR APPLICATION TO THE EVALUATION OF A RUBBER–CARBON BLACK SYSTEM

When one speaks of the properties of a certain rubber-carbon black system, one refers above all to the so-called carbon-black dispersion. There are various possible ways of measuring this dispersion. Electron-optical methods have become especially well known in recent times. The use of an electron microscope for such a test is in most cases impracticable. Moreover, it is doubtful whether all the finest structural characteristics in the entire test material during the slight distension of the carbon black particles can be determined with this apparatus. Even if this were possible, it is still difficult to choose an index which characterizes the optically visible dispersion. Electrical measurements, especially direct-current resistance and loss angle at high frequencies, have been used for a long time to estimate the carbon black dispersion[7]. They have the advantage that direct measurements are obtained, but the disadvantage that the interpretation of the results may be quite difficult. The measurement and evaluation of electrical quantities are the object of further studies, and the technically important system of 100 parts by weight of natural rubber plus 50 parts by weight of CK-IV carbon black has been studied in particular.

Besides the above-mentioned values of the specific resistance, dielectric

constant, and loss angle, the after-effect is especially pronounced in carbon black mixtures. This is the delayed charge and discharge of a condenser, which utilizes the sample as the dielectric. The after-effect is probably the principal cause of the frequency dependence of the dielectric constant and loss angle of the rubber-carbon black system[8].

While the dielectric after-effect in unloaded crude rubber represents an almost immeasurably small potential, the after-effect is increased considerably by the addition of carbon black. This effect was measured with an electrometer-amplifier. This consists of an electrometer tube T116 having anode current-grid voltage compensation. At an initial resistance up to 5×10^{13} ohms, d.c. voltages from zero to 5 volts can be measured on a practically loss-free basis.

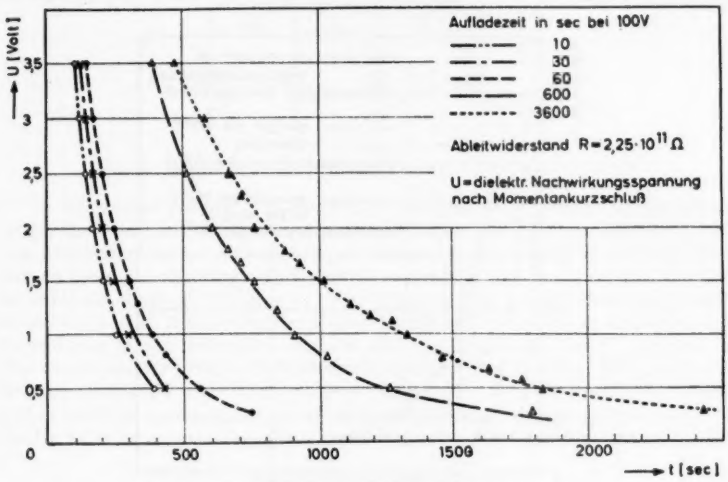


FIG. 1.—Dielectric after-effect for different times of charging.
Charging time in seconds at 100 volts.

10
30
60
600
3600

Insulation resistance $R = 2.25 \times 10^{11}$ Ω. U = dielectric after-effect voltage after momentary short circuit.

A circular test-specimen, of diameter 55 mm. and about 9–10 mm. thick, stamped out of a film, is coated on both sides the size of a circle of 40 mm. diameter, with conducting silver lacquer as the electrode. This sample is subjected to a direct voltage (e.g., 100 v.) for a definite time. After this period, both electrodes are short-circuited about 0.1 second; then the specimen is connected with the electrometer. It is observed that the voltage rises from zero to a maximum very rapidly, and then decreases slowly (see Figures 1 and 2, in which only the descending branch of the curve is shown, since the ascending branch can not be registered exactly, owing to the rapid change of measuring values). This voltage can have measurable values even after a long time, often about 0.1 volt after 1 hour. The voltage at any definite time increases with the previous time of exposure of the polarization voltage, as well as with the value of the resist-

ance connected in parallel with the sample, which consists of the resistance of the specimen and the grid resistance of the electrometer tube. The results can be reproduced well on the same specimen after it is completely discharged. It is striking that greater conductivity of the specimen gives a greater after-effect. An increase of the temperature diminishes the after-effect, and also the conductivity. If the specimen is subjected to internal mechanical stress, e.g., by the application of pressure, the after-effect increases considerably.

A possible explanation of this effect would involve the assumption of carbon dipoles with separate charges. These dipoles rotate under the influence of a polarization field in the direction of the field, and thereby acquire additional charges. After the field is disconnected, the dipoles turn back to their initial position and thus lose their supplementary charges. Now it is very difficult to

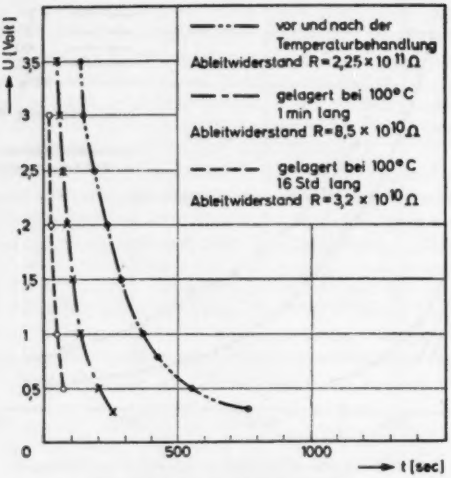


FIG. 2.—Dielectric after-effect for different temperatures of pretreatment. ——— - - ——— before and after heat treatment. Insulation resistance $R = 2.25 \times 10^{11}$ Ω. ——— - ——— heated 1 minute at 100° C. Insulation resistance $R = 8.5 \times 10^{10}$ Ω. — — — — — — heated 16 hours at 100° C. Insulation resistance $R = 3.2 \times 10^{10}$ Ω.

explain how separate charges can remain on a conductive carbon black dipole without any field effect. Moreover, the after-effect and dielectric constant would be expected to decrease during compression of the specimen, owing to a slowing down of the rotation of the dipoles, in contradiction with the experimental results.

In the opinion of the present author, there are many transitions between the two extremes of complete contact and absolute insulation between the carbon black particles, which depend chiefly on the distance and field strength between the particles. This phenomenon may be closely connected with the semiconducting properties of carbon black, which are also responsible for the instantaneous change of conductivity with field strength. If the sample is now subjected to a direct-current voltage, the neighboring carbon black particles which are "coupled" in the direction of the field, with slight conductivity, are charged through a certain resistance. Since each carbon particle has a certain electric

capacity in relation to its surroundings, the capacity is charged through this resistance, and a delay determined by the time constant is observed.

The rather slow discharge of such capacities after short-circuiting causes an after-voltage. Smaller distances between the particles cause large capacities, and therefore, larger after-charges, but greater conductivity at the same time. At higher temperatures, the formation of a resistance-capacity bridge is disturbed by the thermal motion; the conductivity and capacity decrease, and also the after-effect. If the specimen is subjected to mechanical stress, the ordered structure increases and consequently, the after-effect, too, since the mobility of the particles is reduced. The after-effect is therefore essentially a "retarded" capacity, as is represented by the following concepts.

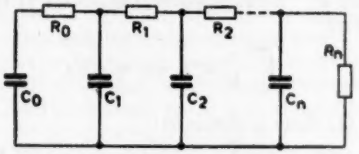


FIG. 3.—General electric-model diagram for the rubber-carbon black system.

In electro-technology, it is customary to represent a definite completed arrangement (vacuum tubes, etc.,) by an equivalent diagrammatic system. This was attempted here. The results of measuring the dielectric after-effect as well as the d.c. resistance and dielectric constant at low frequencies are represented in the diagram in Figure 3. This diagram can, by suitable measurement, be so drawn that it includes the dielectric after-effect as well as the frequency dependence of the dielectric constant and loss angle and the d.c. resistance. The model can be further simplified, so that only one parallel- and one series-resistance-capacity unit remains (see Figure 4). Such a simplified scheme makes possible an exact mathematical treatment and later a comparison of the results with practical after-effect measurements. In this diagram, U is the

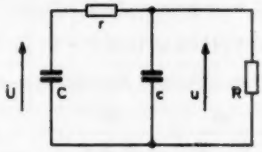


FIG. 4.—Simplified electric-model diagram for the rubber-carbon black system.

voltage at the electrodes. In the model with the symbols indicated the following relations hold true:

$$u = U + Cr \cdot \frac{dU}{dt} \text{ (voltage)} \tag{1}$$

and

$$-c\frac{du}{dt} = \frac{u}{R} + C\frac{dU}{dt} \text{ (current)} \tag{2}$$

Combination of Equations (1) and (2) gives a differential equation of the second order for the potential U. For the sake of simplification, auxiliary symbols are introduced for the individual time constants: $cR = v$ (loss-time constant).

$Cr = n$ (after-effect-time constant). $CR = 1$ (loss of charge-time constant).

$$vn \cdot U'' = (n + v + 1)U' + U = 0 \tag{3}$$

The general solution has the form:

$$U = k_1 e^{-at} + k_2 e^{-bt} \tag{4}$$

At time $t = 0$, let $U = U_0$. Then

$$U_0 = k_1 + k_2 \tag{5}$$

The other equations for the integration constants are derived from the charging balance. After an infinitely long time, the total charge has discharged through the resistance R. Now, however, the charge at time $t = 0$ is equal to $cu_0 + CU_0$. Therefore:

$$\int_0^\infty \frac{u}{R} \cdot dt = cu_0 + CU_0 \tag{6}$$

Combining (1) and (4) there is obtained:

$$\int_0^\infty u \cdot dt = \left[nU - \frac{k_1}{a} \cdot e^{-at} - \frac{k_2}{b} \cdot e^{-bt} \right]_0^\infty \tag{7}$$

from which follows:

$$\frac{k_1}{a} + \frac{k_2}{b} = vu_0 + (1 + n)U_0 \tag{8}$$

Thus the general potential equation for U is:

$$U = \frac{ab}{b - a} \left\{ \left[\left(1 + n - \frac{1}{b} \right) U_0 + vu_0 \right] e^{-at} - \left[\left(1 + n - \frac{1}{a} \right) U_0 + vu_0 \right] e^{-bt} \right\} \tag{9}$$

If this system is subjected to a polarization voltage U_p for a sufficiently long time and short-circuited at C, then at time $t = 0$, $U_0 = 0$ and $u_0 = U_p \cdot \frac{R}{R + r}$. The following formula is thus obtained for the after-effect.

$$U_n = \frac{ab}{b - a} \cdot vU_p \cdot \frac{R}{R + r} (e^{-at} - e^{-bt}) \tag{10}$$

Determination of the coefficients a and b gives

$$a = \frac{(v + n + 1) - \sqrt{(v + n + 1)^2 - 4 \cdot vn}}{2 \cdot vn} \tag{11}$$

and

$$b = \frac{(v + n + 1) + \sqrt{(v + n + 1)^2 - 4 \cdot vn}}{2 \cdot vn} \tag{12}$$

The after-effect voltage U_n increases from zero very rapidly to a maximum and then falls very slowly toward zero. The courses of the calculated and experimental curves are in most cases in good agreement, although the experimental values for one sample at long intervals are somewhat greater than the

calculated values. This can be explained by the fact that, in the calculation, the terms following the first after-effect term can be disregarded. This is obviously true only at relatively long times of measurement. Encouraged by this discovery, we tried to use the same model in a practical system in the audio frequency range.

When it was found that measurements at lower frequencies were especially important, it became necessary to look for practical methods of measurement. Because of the high losses of carbon-black mixtures, precise measurements of the dielectric constant and loss angle are quite problematic, even at medium audio frequencies, simply because no practical bridge minimum can be maintained. It is known that, from a purely technical viewpoint, the determination of the loss angle is based on the determination of a capacity and a resistance in series or parallel connection. If the rubber-carbon black system really corresponds to such a scheme, a definite minimum would have to appear in the bridge member of the system, even with great losses. An exact minimum means that, in every phase of current or voltage, the indicating instrument reads zero. In particular, when the inertialess magic eye is used as indicator of bridge balance, there is no setting of the resistance and capacitance standards that will give an absolute zero voltage for each instantaneous voltage in low frequency measurements on samples with high carbon black. Nor, according to the model system

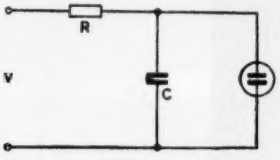


FIG. 5.—Principle of the production of relaxation oscillations in series connection.

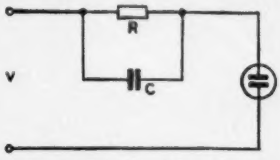


FIG. 6.—Principle of the production of relaxation oscillations in parallel connection.

presented, is this to be expected. Rather, a system having the same structure as the test-specimen must be present in the control branch of the bridge; only then would an absolute minimum be attained, i.e., the magic eye would become wide open. What has been said of the angle loss is equally true of the measurement of the dielectric constant. Moreover, with sinusoidal alternating currents, in the passage through the instantaneous-voltage zero, the non-linearity of the resistances and capacities of the rubber-carbon black system is most disturbingly evident.

Proceeding from these considerations, an experimental hook-up was assembled, in which the capacity was determined from relaxation oscillations. A condenser C was charged through a resistance R by a high direct-current voltage V (about 200 v.). Parallel to this condenser was a neon tube or a thyraton. When the voltage at the condenser reaches the illumination voltage of the discharge tube, the latter is lighted and discharges the condenser to the extinguishing voltage. Next, the tube is extinguished, and the condenser is charged again (see Figure 5). In addition to this series-hook-up of resistance and condenser, a parallel connection is possible (see Figure 6). In this system, relaxation oscillations of serrated form are observed. For an ideal condenser, the following frequency equation applies to both series and parallel connections:

$$\frac{1}{f} = RC \cdot \ln \frac{V - U_1}{V - U_2} \tag{13}$$

Here f is the frequency, U_1 is the extinction voltage, and U_2 is the lighting voltage of the tube.

The circuit can easily be so arranged that by means of a commutator measurements can be made in the same apparatus in both parallel and series connection. By comparing the capacity to be measured in substitution hook-up with a standard, measurements accurate to at least 1 per cent can be made. The frequency comparison can be made by means of earphones, but is much clearer and more precise when a cathode-ray oscillograph is used, with which, moreover, the exact shape of the curve is also seen. Under these conditions, the high-loss capacities of rubber carbon-black test-specimens often show numerous deviations from a strict serrated form. The frequency comparisons can then be made with the same accuracy, even with high losses; experimental errors are slight under all conditions. Another advantage is the fact that the test-specimen is always under a direct-current voltage polarization, so that

Model hook-up for the specimen at 1000 cycles per second.

$c = 17.5$ pF* $\quad c = 122$ pF*

$R = 60$ MΩ $\quad r = 1.1$ MΩ

*1 pF = 10^{-12} farad.

FIG. 7.—Sample arranged in parallel connection, at 1000 cycles per second.

FIG. 8.—Model arranged in parallel connection, at 1000 cycles per second.

FIG. 9.—Normal capacity (82 pF), at 1000 cycles per second.

during the oscillation phases there is no transition through zero voltage, and, therefore, no greater non-linearities appear.

If a model in accordance with Figure 4, instead of a pure condenser, is used as the standard, a form of curve similar to that of the specimen can be obtained on the oscillograph screen by corresponding adjustments of the resistances and condensers of this model. No absolute agreement is found, but at least a close approximation of the character of the curves of the model and test-specimen. As an example, the frequency curves of such a model hook-up and those of the corresponding test-specimen, which was measured at 1000 cycles per second, are given for the tone frequency range. For the curves of the test-specimen and model hook-ups for various relaxation oscillations see the oscillographs of Figures 7–14.

FIG. 10.—Sample arranged in series connection, at 1000 cycles per second.

FIG. 11.—Model arranged in series connection, at 1000 cycles per second.

The measurements were made without phase compensation, in order to avoid errors from compensation elements. It is evident that the capacity values for the actual sample and for the model follow each other closely within a certain frequency range. Here it must be realized that the model could not be adjusted more accurately, because the standard resistances necessary for the high resistances in parallel were not available. It is of interest to note that C corresponds to the capacity of the test-specimen at high frequency (1000 cycles per second). The parallel resistance, R, is equal to the direct-current resistance. This example shows that, at higher frequencies, only a few elements of the general model are involved in the measurement, whereas, at lower frequencies, more and more elements of the system influence the experimental results. This influence always causes an increase of capacity.

In order to show the differences, determined by the form of the curves of the test voltages used, the measurements of two carbon-black mixtures at various frequencies are reproduced in Figures 7 to 14.

For these measurements, samples with relatively high specific resistances were chosen, since otherwise the measurements would yield very inexact values for a sinusoidal alternating current. In the relaxation oscillation measurements, it is easy to determine whether the resistance of the test-specimen itself plays any part in the experimental result by making measurements first in series and then in parallel hook-up. If no difference is found, then the resistance of the test-specimen has no influence on the results; in case of any possible differ-

FIG. 12.—Samples arranged in parallel connection, at 400 cycles per second.

FIG. 13.—Model arranged in parallel connection, at 400 cycles per second.

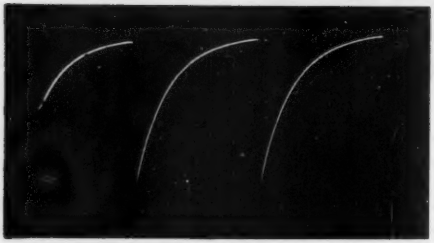


FIG. 14.—Normal capacity (107.8 pF), at 400 cycles per second.

ences, the resistance of the test-specimen and the true capacity can be calculated from the operating voltage in series and parallel connection which give the same frequency. A resistance of 5 megohms was in most cases used as the experimental resistance. With this resistance, resistances greater than approximately 5×10^8 ohm have no influence on the measured capacity.

The data in Table 3 show that the relaxation oscillation method gives higher capacity values, particularly at lower frequencies. This relation can change in samples with higher conductivity, subject to heavy losses, so that the sine measurements indicate larger capacities.

TABLE 2

FREQUENCY DEPENDENCE OF MODEL AND TEST–SPECIMEN WITH A SINUSOIDAL ALTERNATING CURRENT

Frequency (cycles per second)	Capacity of the Model (pF)	Capacity of the Sample (pF)
50	150	200
200	130	165
500	120	125
1000	95	95
2000	45	50

In addition to the above-mentioned measurements of mixtures in the unstressed state, measurements of great significance were also made on mechanically stressed samples. The test-specimen was placed in a circular plate screw condenser and measured without mechanical stress; then the specimen

TABLE 3

	Specific direct-current resistance in Ω per cm.		Dielectric constant for various cycles per second			
			20	100	500	2500
Batch I	2.86×10^{10}	Sinusoidal	27.2	20.9	18.7	11.3
		Trip	49.8	29.8	16.2	11.6
Batch II	1.7×10^{10}	Sinusoidal	32.6	23.5	17.0	12.6
		Trip	47.0	29.0	17.6	12.1

was compressed 20 per cent by turning the screw spindle, and was measured again. The operation was repeated in a third position, i.e., with 40 per cent compression. In these measurements, both the resistance and the capacity of the specimen were measured. A typical example follows.

TABLE 4

CHANGE OF ELECTRICAL CONSTANTS BY STRESS WITH AND WITHOUT STORAGE OF SPECIMEN 16 HOURS AT 100° C

	Specific resistance and dielectric constant at 750 cycles per second and compression of sample		
	0%	20%	40%
Dielectric constant without hot storage	17.9	18.6	20.5
Specific resistance in Ω per cm. in hot storage	2.86×10^{9}	1.96×10^{11}	4.9×10^{10}
Dielectric constant after hot storage	31.4	17.1	17.6
Specific resistance in Ω per cm. after hot storage	1.72×10^{9}	1.2×10^{11}	8.6×10^{10}

Four different test-specimens were died out from the same sheet for these measurements, since an individual specimen could not be used for a second measurement after being highly stressed.

From this series of measurements, it follows that the dielectric constant is increased by compression, while the resistance in most cases is increased by slight stress, but diminished by higher stressing. Hot storage causes a sharp increase of the constant; however, the constant falls greatly when the test-specimen is stressed, and in most cases below the final value of the specimen which has not been heat-treated. These changes of the electrical properties are the result of changes of the carbon-black structure. If the ratio of length to thickness of a carbon-black particle is designated as the *form factor*, then the dielectric constant increases with this form factor. Now several carbon-black particles can become united through flocculation to form a longer chain. This phenom-

enon is also manifest by an increase of the dielectric constant. On the other hand, weak carbon-black chains are destroyed by stress, resulting in a decrease of the dielectric constant and conductivity. When the specimen is compressed, these opposing tendencies come into conflict. On the one hand, there is a tendency toward a stiffening of the structure as a result of an increase of the order of the structure by mechanical tension (decrease of mobility); on the other hand, there is a tendency toward destruction of weak chains as a result of the shearing forces. Measurement of the dielectric constant under stress shows which tendency is dominant. It may rightfully be concluded that a strong increase of the dielectric constant with compression indicates a tight structure, whereas a decrease of the constant under stress indicates a weak chain structure. Bearing this in mind, the experimental values are easily understood. In the unconditioned state, the dielectric constant increases, since mechanical stress stiffens the specimen to a considerable degree. By storage at elevated temperature, considerable flocculation of the carbon-black particles sets in (increase of the dielectric constant of rest). These floccules of carbon-black particles are very weak, however, and are destroyed by relatively small stresses; hence, the sudden fall of the dielectric constant at about 20 per cent compression. It is of interest also that the final value of the constant of the heat-treated sample is smaller that that of the untreated sample. The reason for this lies in the fact that the carbon black particles agglomerate at elevated temperatures. This agglomeration phenomenon can be interpreted in the following way.

At elevated temperatures, the carbon black particles undergo considerable thermal motion. Now the affinity of the carbon-black particles toward one another is very strong, and the probability that two particles, because of their mean field of motion, will meet is relatively great. Since the heat movement is random, the formation of globular agglomerates is favored. This process diminishes the form factor of the carbon-black agglomerates and, therefore, their contribution to the dielectric constant. At any rate, the dielectric constant of a relaxed sample is increased considerably by loose combination of such individual aggregates. However, this increase of the dielectric constant is made completely reversible by a slight stress, since the cohesion of the aggregates is relatively slight.

The foregoing statements are true also of the resistance. The latter is, however, of much less importance in such considerations, because, in this case, the only influence is that of particles which are in random statistical contact and in conductive contact with the electrodes. Carbon-black particles which are insulated in the rubber matrix do not contribute to the total conductivity. In the case of the dielectric constant, the situation is different. There, too, insulated particles are present which can be electrically "seen", and contribute to the final observed behavior of the distribution. For this reason, dielectric-constant measurements were considered to be of particular importance in any study of the carbon-black structure. The direct-current resistance serves only as a completion of such a study. In many cases, however, it can provide valuable additional information.

For the measurement of the dielectric constant, it is important that measurements be made at low frequencies[1]. A high frequency of measurement is easy to control, and gives satisfactorily reproducible values, but only very slight differences between the individual test-specimens, since the measurement involves only the highly conductive range of a carbon-black aggregate. The lower the frequency during the measurements, the larger is the range involved. At audio frequencies below approximately (1000 cycles per second), the dielec-

tric constant increases progressively as a result of the fact that electrical oscillation covers a larger region around a highly conductive nucleus. In the audio-frequency range, the influence of different methods of mixing, temperatures of mixing, etc., on the dielectric constant are considerable.

Determinations of the dielectric constant by relaxation oscillations have, in addition to greater precision, the great advantage that the test-specimen is not subjected to a previously generated oscillation, but takes part itself in an oscillating system. This makes possible an accurate study by an oscillograph, of the influence of the test-specimen on the form of the curves. This in turn makes possible the numerical derivation, from resistance and capacity data, of a model of the rubber sample being studied, which, within the frequency range studied, has electric characteristics similar in all respects to those of the rubber mixture itself.

With such a model, a rough concept of the orientation of carbon-black particles in the rubber matrix is obtained. Here three important cases must be distinguished, which usually are confused in practice.

1. Carbon black is dispersed perfectly uniformly throughout the specimen. The measured dielectric constant is low, and the after-effect is very slight.

Figure 4: C = small, r = very large.

2. The dispersion consists of large aggregates, in which the individual particles often have no definite electric contact with one another. The dielectric constant is still relatively small, but the after-effect is considerable.

Figure 4: C = somewhat larger, r = medium value;
c = relatively large; R = variable.

3. The carbon-black particles form firm chains with large form factor, and are dispersed uniformly in the rubber matrix. The dielectric constant is large, but the after-effect is slight.

Figure 4: C = large; r = very small;
c = large; R = variable.

It is seen that the differences of the dielectric constant depend principally on r, the "coupling resistance", and, to a smaller degree, on changes of C, c, and R. The measured capacities and resistances for the model depend on the shape of the test-specimen. If specific values are in question, the time constants: $c \cdot R = v$, $C \cdot r = n$, and $C \cdot R = 1$, as well as the specific direct-current resistance are calculated.

Rubber mixtures whose characteristics conform to case (3) above give, when vulcanized, high modulus values. Mixtures having lower dielectric constants but very high direct-current resistance show, almost without exception, relatively low modulus values after vulcanization. These characteristics were found to be true, in particular, of the natural rubber-carbon black (CK-IV) system, but they are, in general, also characteristic of other systems.

REFERENCES

[1] Dalbert, *Rev. gén. caoutchouc* **29**, 515, 588, 649 (1952).
[2] Sperberg, Popp, and Biard, *Rubber Age* (N. Y.) **67**, 561 (1950).
[3] Hollmann, *J. Applied Physics* **21**, 402 (1950).
[4] Doede, *Rubber Age* (N. Y.) **69**, 60 (1951).
[5] Debye, "Polare Molekeln", Leipzig, 1929.
[6] Gemant, "Elektrophysik der Isolierstoffe", Berlin, 1930.
[7] Thirion and Chasset, *Trans. Inst. Rubber Ind.* **27**, 364 (1951).
[8] Danzer, *Ann. Physik* **20**, 463 (1934); **21**, 783 (1934–35).

THE MICROSTRUCTURE OF DIENE POLYMERS

I. POLYISOPRENES AND POLYBUTADIENES PREPARED AT HIGH TEMPERATURES *

W. S. RICHARDSON

MELLON INSTITUTE, PITTSBURGH, PENNSYLVANIA

INTRODUCTION

In a previous paper[1] a method has been described by which the microstructure of synthetic polyisoprenes can be deduced from intensity measurements in the infrared spectrum of these polymers. Similar analyses have been made in the case of polybutadienes by Hart and Meyer[2] and by Hampton[3]. It is the purpose of the present paper to present the results of structural determinations on polyisoprenes and polybutadienes prepared by bulk thermal polymerization in the temperature range 100 to 250° C.

EXPERIMENTAL

ANALYSIS OF POLYBUTADIENES

The spectroscopic techniques used in this laboratory for the infrared analysis of polymers are adequately described in the previous paper on the polyisoprenes[1], in which the extinction coefficients for the various types of polyisoprene addition at the characteristic frequencies are tabulated.

For the polybutadienes, it is difficult to find any region where reasonably strong absorption occurs which can be attributed unambiguously to *cis*-1,4-addition. Most polybutadienes show some absorption in the 700 cm.$^{-1}$ region. A part of this is probably due to *cis*-1,4-addition, but it is difficult to establish reliable extinction coefficients from a study of model compounds because of the distressingly large variation both in intensity and frequency among the various models. For this reason, no direct analysis is given for *cis*-1,4-addition. The analysis is made for *trans*-1,4-addition (at 966.5 cm.$^{-1}$) and 1,2-addition (at 910.5 cm.$^{-1}$), and the sum of these concentrations may be subtracted from the made-up concentration of the solution to obtain the *cis*-1,4-concentration. This, of course, assumes that the polymer is linear and has the theoretical unsaturation, and it must be borne in mind that the percentage of *cis*-1,4-addition may be in error if the assumptions are not fulfilled.

The extinction coefficients for *trans*-1,4-addition at 966.5 cm.$^{-1}$ and 1,2-addition at 910.5 cm.$^{-1}$ were established in exactly the same way as those for 1,2- and 3,4-addition in the polyisoprenes[1]. The resulting absolute intensities (A) and peak intensities (α) are given in Table I of reference 1 for the 1,2-addition type of olefins and in the following table for the *trans*-1,4-addition model compounds. A study of the width of the 910.5 cm.$^{-1}$ band in polybutadienes shows that it has the same width as the corresponding band in the polyisoprenes (*viz.*, 8.55 cm.$^{-1}$).

* This work is reprinted from the *Journal of Polymer Science*, Vol. 13. Part I is reprinted from Issue No. 69, pages 229–234, March 1954. Parts II and III are reprinted from Issue No. 70, pages 321–324 and 325–327, respectively, April 1954. The work was done at the Mellon Institute and was supported by the Office of Synthetic Rubber, Reconstruction Finance Corporation.

TABLE I

INTENSITIES OF OLEFIN BANDS, *trans*-1,4-POLYBUTADIENE MODEL COMPOUNDS

Compound	$\nu_{max.}$ (cm.$^{-1}$)	$\left(\frac{\alpha_{max.}}{\text{liter}/\text{cm.} \times \text{mole}}\right)$	$\left(\frac{A}{\text{liter}/\text{cm.}^2 \times \text{mole}}\right)$	$\Delta\nu_{\frac{1}{2}}$ (cm.$^{-1}$)
trans-4-Octene	966	123.5	5930	13.3
trans-2-Hexene	963	153	5750	11.1
Average		*133*	*5840*	*12.2*
"Polymer value"	966.5	133	5840*	12.1

* Assumed.

In addition to the overlap of the 910 and 966 cm.$^{-1}$ bands on each other, a small correction was applied for the overlap of the weaker 995 cm.$^{-1}$ band (due to vinyl groups) on the 966 cm.$^{-1}$ *trans*-1,4-addition band. The calculations lead to the peak extinction coefficients (α) used in the analyses which are given in Table II.

In recording the analyses of polybutadienes, the percentages of *trans*-1,4- and 1,2-addition are reported together with the percentage of *cis*-1,4 by difference from 100 per cent. In the case of the polyisoprenes, all four structures (*cis*- and *trans*-1,4-, 1,2-, and 3,4-additions) are determined and can be summed to give the "found" concentration of the solutions analyzed. The percentages

TABLE II

"POLYMER VALUES" OF EXTINCTION COEFFICIENTS *

Structure	966.5 cm.$^{-1}$	910.5 cm.$^{-1}$
trans-1,4-Addition	133	1.6
1,2-Addition	5.2	149
cis-1,4-Addition	0†	0†

* Units are: liters/mole × cm.
† Assumed.

reported in the case of polyisoprenes are recorded as the percentages of each structure in this "found" concentration, and the "found" concentrations are reported as per cent of the made-up concentrations of the solutions.

PREPARATION OF POLYMERS

The monomer (about 10 grams from which stabilizer had been removed) was contained in a small steel bomb and heated in a thermostated oil bath. The bath was overheated by a calculated amount before the run to aid in bringing the sample to temperature quickly. Reaction times were long compared to heating and cooling times. The polymer was recovered by pouring the cooled monomer-dimer-polymer mixture into methanol, and was purified several times by solution in benzene and precipitation from this solution with methanol.

TABLE III

STRUCTURE OF POLYBUTADIENES

Preparation temp. (° C)	% 1,2	% *trans*-1,4	% *cis*-1,4*
100	21.5	51.2	27.3
127	18.8	44.3	36.9
175	20.4	42.5	37 1
223	17.7	39.4	42.9

* By difference from made-up concentration of solutions.

TABLE IV

STRUCTURE OF POLYISOPRENES

Preparation temp. (° C)	% 1,2	% 3,4	% *trans*-1,4	% *cis*-1,4	% Found
100	5.0	5.9	66.0	23.1	97.9
150	4.6	6.1	72.8	16.5	101
203	2.8	8.8	69.4	19.0	91.2
257	1.8	8.8	77.3	12.1	92.7

The polymer was then dried by the frozen benzene sublimation method; and finally, a solution of known concentration in carbon disulfide was prepared for the spectral studies.

Polybutadienes were prepared at 100, 127, 175, and 223° C; and polyisoprenes were prepared at 100, 150, 203, and 257° C.

RESULTS

The structures of the various polymers are given in Tables III and IV. In order to show the general shape of the dependence of structure on polymerization temperature, Figures 1 and 2 include some points (indicated by squares) in the temperature region −20 to 120° C which have been previously published, or which add nothing new to the work of Hampton[3].

The polybutadienes show the expected leveling off of the *cis*-1,4- and *trans*-1,4-addition with increasing polymerization temperature; the final structure tends to about 20 per cent, 1,2-addition and 40 per cent each of *cis*- and *trans*-1,4-addition. These results can be represented quite adequately by an Arrhenius type relationship:

$$RT \log R_{ij} = -\Delta H_{ij} + T\Delta S_{ij}$$

where R_{ij} is the ratio of the concentration of structure i to structure j, and ΔH_{ij}

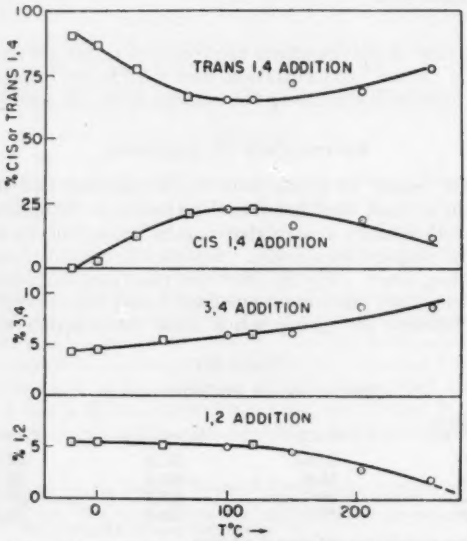


FIG. 1.—Structure of polyisoprenes *vs.* preparation temperature.

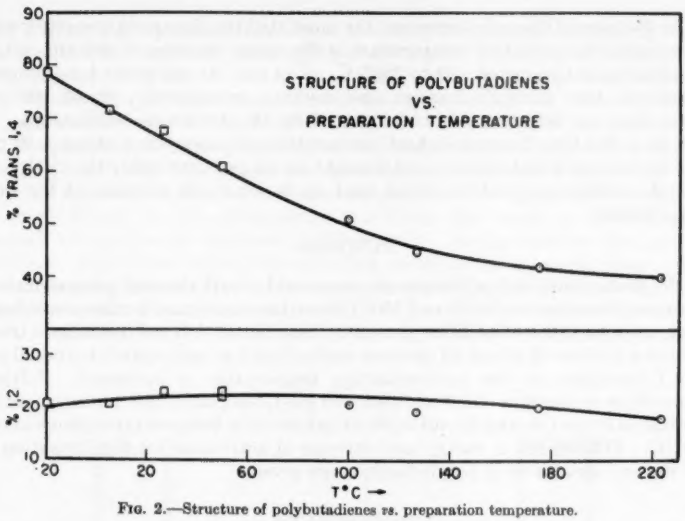


FIG. 2.—Structure of polybutadienes *vs.* preparation temperature.

and ΔS_{ij} are the differences in energy of activation and entropy of activation for their formation. This is shown graphically in Figure 3 from which:

$$\Delta H_{trans} - \Delta H_{cis} = -3200 \text{ cal.}$$
$$\Delta S_{trans} - \Delta S_{cis} = -6.5 \text{ e.u.}$$
$$\Delta H_{trans} - \Delta H_{12} = -770 \text{ cal.}$$
$$\Delta S_{trans} - \Delta S_{12} = -0.37 \text{ e.u.}$$

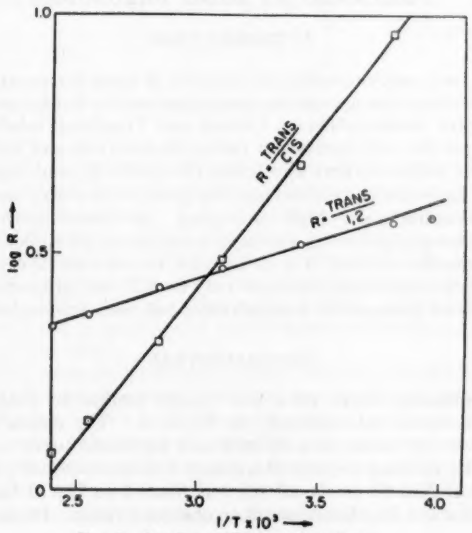


FIG. 3.—Log R *vs.* $1/T$ for polybutadienes.

In the case of the polyisoprenes, the most striking change in structure with increasing polymerization temperature is the rapid decrease of the amount of 1,2-addition in the region 100 to 250° C. The *cis*-1,4- and *trans*-1,4-additions apparently pass through maxima and minima, respectively, about 100° C. These data are not amenable to treatment by the Arrhenius relationship. It may be noted that the two highest temperature polymers show about a 10 per cent decrease of unsaturation, and it might be argued that either the *cis*-1,4- or the 1,2-addition (or both) is being used up in some side reaction at the high temperatures.

SYNOPSIS

Polybutadienes and polyisoprenes prepared by bulk thermal polymerization at temperatures between 100 and 250° C have been analyzed for the percentages of the various types of addition present. It is found that polybutadiene tends toward a mixture of about 40 per cent each of *cis*-1,4- and *trans*-1,4- and 20 per cent 1,2-addition as the polymerization temperature is increased. Polyisoprenes show a decrease of 1,2-addition and *cis*-1,4-addition and a corresponding increase in *trans*-1,4- and 3,4-addition at preparation temperatures above about 100° C. Differences in energy and entropy of activation for the formation of the various structures in polybutadiene are given.

REFERENCES

[1] Richardson and Sacher, *J. Polymer Sci.* **10**, 353 (1953).
[2] Hart and Meyer, *J. Am. Chem. Soc.* **71**, 1980 (1949).
[3] Hampton, *Anal. Chem.* **21**, 923 (1949).

II. POLYISOPRENES AND POLYBUTADIENES PREPARED AT HIGH PRESSURES

INTRODUCTION

The rapid bulk polymerization of isoprene at room temperature under high hydrostatic pressure was apparently first observed by Bridgman and Conant[1]. A more extensive investigation by Conant and Tongberg[2] established the free radical nature of the polymerization (peroxide catalysis and hydroquinone inhibition). The latter workers also noted the solubility and elasticity of polymers made to moderate conversion and the insoluble crumbly nature (gelation) of the polymers made to very high conversion. In view of the well known effect of increased pressure in driving chemical reactions in the direction of the products of least specific volume, it is of interest to consider the possibility that diene polymers made at high pressures may be different in microstructure from polymers made at comparable temperatures but near atmospheric pressure.

EXPERIMENTAL

The high-pressure bomb used was closely similar to that described by Adams[3], and is shown schematically in Figure 1. The piston (a) was forced into the cylinder by means of a 20 inch ram hydraulic press equipped with a manostat. The packing consists of a snugly fitting section of a rubber stopper (b). A layer of No. 40 motor oil (c) was floated on top of the transmitting fluid (d), which was a 50:50 mixture of alcohol and water. During the course of

long polymerization runs, there was a tendency for the rubber packing to be extruded out between the piston and cylinder wall. This layer of rubber made it exceedingly difficult to remove the piston after the pressure was released. Therefore a shoulder was included near the top of the piston, which could be gripped with a screw driven "puller" to aid in the removal of the piston.

The pressure of the polymerization runs was determined by calibrating the internal bomb-pressure against the Bourdon gauge on the press. This was done by means of a small stainless steel pieziometer, the design of which is shown in Figure 1. The pieziometer was filled with water by assembling it beneath the surface of degassed distilled water, taking care to eliminate all bubbles. About 3 cc. of mercury was then added to the upper chamber. The hole connecting the two chambers was made with a No. 70 drill and was large enough to pass mercury easily under pressure, but small enough so that normal jarring and bumping did not shake the mercury through. When the pieziom-

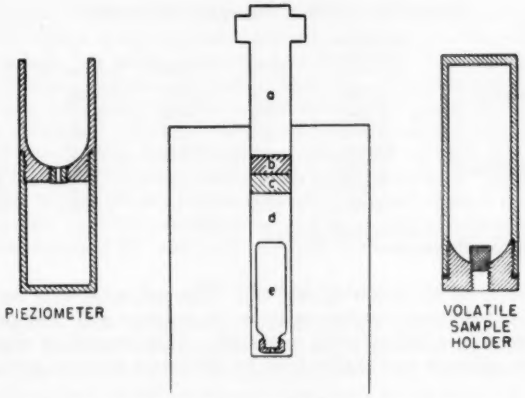


FIG. 1.—Apparatus for the preparation of high-pressure polymers.

eter was contained in the bomb and subjected to high pressure, the mercury passed through the small hole connecting the two chambers as the water in this lower chamber was compressed. From the known compressibility of the steel, mercury, and water, and the weight of trapped mercury, the pressure could be calculated. It was generally found that the pressure within the bomb was from 10 to 20 per cent less than that calculated from the gauge and the press and bomb dimensions. This frictional loss in the packing, while substantial, was quite reproducible and in general the pressure measurements may be taken as good to about ± 5 per cent.

The monomers were Phillips "pure grade" and were distilled prior to use. Eastman Kodak Company benzoyl peroxide was used as a catalyst, without additional purification. The catalyst concentration in all runs was about 0.2 mole per cent. All polymerizations were made at room temperature.

In the cases where isoprene was the monomer, the sample container was simply a small glass vial with a plastic screw cap. A small hole was drilled in the cap, and this was screwed down on a thin disc of lead foil which sealed the

tube. This arrangement did not leak when inserted upside down in the bomb, but the seal was easily ruptured when pressure was applied.

For monomers, such as butadiene, which boil below room temperature, the sample holder shown in Figure 1 can be used. This consists of a stainless steel tube one end of which is fitted with a screw cap which can be screwed in hard enough to give a vapor-tight seal. The center of this cap is tapped with a hole large enough to accommodate a small cork on the inside; the cork is waxed in place before the holder is filled. This container will hold butadiene at room temperature for several hours, but the cork is easily dislodged by the application of external pressure in the bomb.

After a few trial runs to obtain crude rate of polymerization data, the polymers listed in Table I were prepared at conversions between 50 and 75 per cent. This involved runs of about three days at 5700 kg./sq. cm., but only about six

TABLE I

STRUCTURE OF HIGH PRESSURE POLYMERS *

Polymer	Preparation pressure, kg./cm.²	% 1,2	% 3,4	% *trans*-1,4	% *cis*-1,4
Polyisoprene	5,700	5.9	6.7	85.5	1.9
	7,800	5.9	6.8	84.7	2.6
	9,000	6.7	7.8	85.5	0
	10,000	6.9	6.9	86.2	0
Polybutadiene	5,700	13	—	44	43†
	7,600	17.5	—	57.3	25.2†
	10,000	17.3	—	51.7	31.0†

* Bulk, 30° C, 0.2 mole per cent benzoyl peroxide.
† By difference from 100 per cent.

hours were required at 10,000 kg./sq. cm. The polymers were recovered by dissolving the monomer-polymer mixture in benzene and precipitating the polymer from this solution with methanol. This procedure was repeated twice, and the polymer was finally dried by the frozen benzene method.

RESULTS

The polyisoprenes were all 100 per cent soluble in benzene and were tough elastic materials of high molecular weights. The polybutadienes, on the other hand, generally contained some gel, although this did not exceed about 10 per cent provided the conversions were kept below 75 per cent. When this gel was removed, the polybutadienes were physically similar to the polyisoprenes.

The polymers which have been analyzed, and the pressures at which they were prepared, are listed in Table I.

The spectroscopic methods used in the analysis of the polymers have been described elsewhere[4].

As can be readily seen, there are no large systematic changes of structure as a function of pressure within this pressure range. The polyisoprenes recorded here are very similar in structure to emulsion polymers prepared at subzero temperatures at atmospheric pressure[5]. In the case of the polybutadienes, if the percentage *cis*-1,4-addition, obtained by difference, is significant, the structures are similar to high-temperature bulk or emulsion polymers[6]. It should be borne in mind, however, that the percentages of *cis*-1,4-addition may be in error if cyclization or other types of side reactions are occurring. In

general, it may be said that high-pressure polymerization (in this pressure range) leads to microstructures which are not drastically different from those obtainable by bulk or emulsion polymerization at atmopsheric pressure.

REFERENCES

[1] Bridgman and Conant, *Proc. Natl. Acad. Sci. USA* **15**, 680 (1929).
[2] Conant and Tongberg, *J. Am. Chem. Soc.* **52**, 1659 (1930).
[3] Adams, *Rev. Sci. Instruments* **7**, 174 (1936).
[4] Richardson and Sacher, *J. Polymer Sci.* **10**, 353 (1953); Richardson, *J. Polymer Sci.* **13**, 229 (1954).
[5] Richardson and Sacher, *J. Polymer Sci.* **10**, 353 (1953).
[6] Hampton, *Anal. Chem.* **21**, 923 (1949); Richardson, *J. Polymer Sci.* **13**, 229 (1954).

III. POLYISOPRENES AND POLYBUTADIENES PREPARED WITH CATIONIC CATALYSTS

INTRODUCTION

It is well known that catalysts of the Friedel-Crafts type cause the polymerization of diene monomers and that this reaction is ionic rather than free radical in nature. It is also known that such catalysts cause diene polymers to isomerize (cyclize), and one may expect that the polymerization and isomerization reactions will occur simultaneously during the preparation of polymers with these catalysts. While considerable information is available describing methods of preparation and the general properties of such polymers[1], there seem to be few or no data concerning their microstructures. It is the purpose of this paper to present the results of such structural studies (obtained from infrared spectra) on seven polyisoprenes and three polybutadienes, prepared at temperatures between 30° and −78° C, with various cationic catalysts.

EXPERIMENTAL

The polymers were prepared in the following ways. The catalyst (~2 mole per cent, based on the monomer) was dissolved in the diluent (50 per cent by volume based on monomer) and precooled to the polymerization temperature. This was then added slowly, with shaking, to the cooled monomer, and when the addition was completed, the mixture was shaken at the polymerization temperature until a conversion of about 50 per cent was reached. In the case of the very fast reactions, this conversion was sometimes exceeded before the reaction could be stopped. No special precautions were taken to avoid moisture other than keeping the reaction vessels closed whenever possible. The polymers were recovered by pouring the reaction mixture into cold methanol and quickly collecting the polymer and dissolving it in benzene. The polymers generally contained some gel, which was removed by filtration, and the soluble portion was purified several times by solution in benzene and precipitation with methanol. Finally, the polymers were dried by the frozen benzene method, and carbon disulfide solutions of known concentration were prepared for spectral analysis.

The techniques used in the infrared analysis of polyisoprenes and polybutadienes have been described elsewhere[2].

RESULTS

The results of the analyses of seven polyisoprenes and three polybutadienes are given in Table I. Also recorded are the polymerization temperature, the

TABLE I

STRUCTURE OF CATIONIC POLYMERS

Polymer	Prepn. temp. (° C)	Catalyst	Solvent	Rate*	% 1,2	% 3,4	% *cis*-1,4	% *trans*-1,4	% found	Physical appearance
Polyisoprene	30	BF_3	Pentane	2 days	3.4	6.1	0	90.5	74.0	Tacky solid
	30	BF_3	Pentane	8 days	4.0	7.1	0	88.9	51.2	Crumbly solid
	30	$SnCl_4$	$CHCl_3$	2 hours	3.9	5.7	0	90.4	50.2	Tacky solid
	−20	$SnCl_4$	$CHCl_3$	1 hour	4.3	4.0	0	91.7	79.8	Rubbery
	−45	$SnCl_4$	$CHCl_3$	4 hours	6.1	5.1	0	88.8	82.3	Crumbly solid
	−78	$AlCl_3$	EtBr	~5 min.	3.2	3.7	0	98.1	59.2	Crumbly solid
	−78	$SnCl_4$	None	15 min.	7.2	5.8	0	87.0	74.2	Crumbly solid
Polybutadiene	30	$SnCl_4$	$ChCl_3$	2 days	7.6	—	—	28.3	35.9	Tacky solid
	−30	$AlCl_3$	EtBr	15 min.	4.8	—	—	12.4	17.2	Crumbly solid
	−78	$AlCl_3$	EtBr	10 min.	7 1	—	—	21.5	28.6	Crumbly solid

* Approximate time to 50% conversion.

diluent, the approximate time to 50 per cent conversion, and, crudely, the physical appearance of the polymers. In the case of the polyisoprenes, where an independent determination of each of the four types of addition is made, the percentages of the four structures are normalized to total 100 per cent, and the "% found", which may be taken as the unsaturation, is recorded. In the case of the polybutadienes, no analysis is made for *cis*-1,4-addition, so the percentages of 1,2-and *trans*-1,4-addition are given and their sum is recorded as "% found". In these polymers, it is unlikely that the difference between the "% found" and 100 per cent can be taken as *cis*-1,4-addition.

With regard to the structural data, it is hardly sufficient to draw any significant conclusions, aside from the obvious facts that the polymers appear to lack the theoretical unsaturation and that the distribution of the various types of addition, i.e., the ratios among them, are not drastically different from the free radical type of ploymers. Within the two groups, there seems to be no systematic changes in structure with polymerization temperature. Unfortunately, at the present state of these studies, the infrared spectra provide no clue as to the nature of the remaining structures in these polymers.

SYNOPSIS

A number of polyisoprenes and polybutadienes have been prepared at temperatures between 30° and −78° C, using Friedel-Crafts catalysts. Quantitative analyses of the various types of addition occurring in these ploymers have been made from their infrared spectra. It has been found that the linear structures corresponding to 1,4-, 1,2- and 3,4-addition are present in about the same ratios as in the free-radical type of polymers. However, in the case of the polyisoprenes (and apparently also the polybutadienes), these structures account for only about 50 to 75 per cent of the material present.

REFERENCES

[1] Marvel *et al.*, *J. Polymer Sci.* **6**, 483 (1951).
[2] Richardson and Sacher, *J. Polymer Sci.* **10**, 353 (1953); Richardson, *J. Polymer Sci.* **13**, 229 (1954).

SPONTANEOUS CONTRACTION OF RUBBER. II. SPONTANEOUS CONTRACTION OF RUBBER AND ITS DEPENDENCE ON THE CONDITIONS OF TESTING, AND SOME FACTORS CONCERNED IN COMPOUNDING AND TECHNOLOGY *

M. M. Reznikovskiĭ and M. K. Khromov

Scientific Research Institute of the Rubber Industry, Moscow, USSR

INTRODUCTION

The importance of the rate of spontaneous contraction in the determination of the properties of technical rubber mixtures has already been pointed out in a previous article[1]. An approximate theory of spontaneous contraction, accounting for relaxation and internal friction of rubber, was given at that time.

In the present study, data obtained in an experimental study of the rate of spontaneous contraction and its dependence on the test conditions (deformation, temperature, time that the specimen remains stretched, type of rubber and compounding ingredients, and time of vulcanization) are presented and discussed. Unloaded vulcanizates of isoprene rubber (smoked sheet), butadiene rubber (SKB), and butadiene-styrene rubber (Buna S-3) were chosen as materials for this study. These were vulcanized in a press at 143° C. The time of vulcanization was varied.

EXPERIMENTAL TECHNIQUE

The apparatus for the study of spontaneous contraction of rubber is shown schematically in Figure 1.

In Figure 1, the rubber test-specimen (1), in the form of a strip 120 mm. long, is passed through the horizontal slot (2) in the light duralumin frame (15), and its ends are fastened in the clamp (3). The frame (15) moves vertically in the guides (4). The initial deformation of the rubber is measured by lowering the frame with a moveable screw (5), which is connected with a chain and moved by turning the detachable nut (10). After the desired elongation of the test-specimen has been reached, the elastic stress is determined with a lever dynamometer (7), which is connected with the upper clamp (3). This stress can be determined within an accuracy of 1 per cent by decreasing the weight (8) before the stylus (9) begins to deviate from the position of equilibrium. Because of the relaxation, the stress thus measured is a function of the time elapsed from the beginning of the experiment.

For recording the movement of the frame (15) during spontaneous contraction, a thin steel needle (14) is used, which with its blackened point touches the surface of a metallic drum (11), which is rotated by a commutator motor (12). The rotation of the drum, by recording the progress of the contraction phenomenon as a function of time, makes it possible to construct a time-displacement graph, in which the time scale is represented by the rate of rotation of the drum.

* Translated for Rubber Chemistry and Technology from *Kolloidnyi Zhurnal*, Vol. 14, No. 5, pages 357–366 (1952).

For the determination of the rate of distribution of impulse, a second frame with a recording needle is used, which is attached to the top of the test-specimen, near the stationary clamp (not shown in the diagram). Designating the distance between the recording instruments by L_0', which represents the moment of initiation of motion of the upper frame (see Figure 1 (15)), and by L_0 the same distance in an undeformed test-specimen, we have for the permanent momentary residual deformation:

$$\vartheta = \frac{L_0' - L_0}{L_0} \tag{1}$$

The beginning of spontaneous contraction is measured by the moment of sudden rotation of the moveable screw (5), which then frees the frame (15) from the clamp (6). The initial deformation is determined by the marks on the test-specimen and by reading the displacement scale (16). The curve of spontaneous contraction is transcribed on millimetric paper with the vertical displacement scale (16) and horizontal time scale (17). For studying the temperature variations, the test-specimen is enclosed, together with the revolving drum, in a special jacket with double walls, between which a liquid fed through an ultrathermostat is circulated.

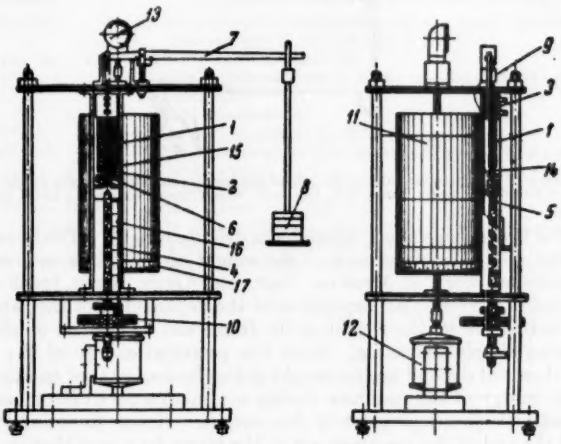


FIG. 1.—Apparatus for the study of the spontaneous contraction of rubber mixtures (see explanations in the text).

The apparatus described differs as follows from that used in the work of Mrowka, Dart, and Guth[2] in the connection of the apparatus for recording spontaneous contraction with the dynamometer, making it possible to determine the stress in the deformed specimen at the moment preceding contraction, and by means of the thermostat jacket, making possible measurements at different temperatures.

EFFECT OF THE WEIGHT OF THE FRAME

In the preceding article[1], the movement of a strip of rubber during spontaneous contraction was studied without considering the effect of the frame fastened

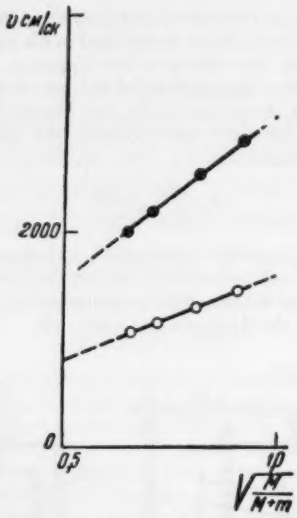


FIG. 2.—Relation of the maximum value of the rate of spontaneous contraction to the weight of the frame. Buna S-3 rubber mixture. ●$\xi_0 = 2.0$; ○$\xi_0 = 1$. The ordinate represents v *in cm. per sec.*

to the end of the test-specimen, which has a definite weight. The linear relation between the rate of contraction and the weight of the frame, assumed in the above-mentioned work of Mrowka, Dart, and Guth, is not justified from a practical point of view. An expression of the dependence of the rate of spontaneous contraction on the weight of the frame can be derived on the basis of the following simple reasoning. Since the potential energy of the deformed specimen does not depend on the weight of the frame fastened to one end of it, the kinetic energy of the specimen during contraction up to the moment when $\xi = 0$ must also be independent of this weight. Hence, denoting the rate of motion of the end of the specimen not in the frame by v, and that in the frame by v_m, and assuming, in accord with the fact established in the preceding work, that the rate of motion of the end when $\xi = 0$ is equal to the rate of motion of the center of the mass of the specimen, we have:

$$\frac{Mv^2}{2} = \frac{(M + m)v_m^2}{2} \tag{2}$$

where m is the mass of the frame.

Solving Equation (2) for v_m, we obtain:

$$v_m = v \cdot \sqrt{\frac{M}{M + m}} \tag{3}$$

As is seen in Figure 2, the experimentally observed dependence of the rate of spontaneous contraction on the mass of the frame is in good agreement with Equation (3).

In these experiments, when the mass of the specimen was 4 grams, the mass of the frame was 0.7 gram. The presence of the frame lowers the rate of spon-

taneous contraction approximately 8 per cent. Later, in evaluating the experimental results, a correction calculated from Equation (3) was introduced in the calculation of the rate.

RESULTS AND DISCUSSION

The method of treating the experimental data based on the conclusions stated in a previous article[1] is summarized in Table 1.

In the study of the influence of these or other variable factors, besides the rate of spontaneous contraction, the corresponding relations for the initial modulus E_0', momentary residual elongation ϑ, and the conventional coefficient

TABLE 1

DESIGNATIONS AND FORMULA FOR CALCULATIONS

Symbols and units of measurement	Meaning of designation and formula for calculation
S_0 (sq. cm.)	area/ square of cross-section of specimen (doubled area of cross-section of rubber strip)
ρ (g. per cc.)	density of rubber sample
L_0 (cm.)	distance between bench marks on undeformed specimen
T (° C)	temperature
	initial deformation
t (min.)	time that specimen remains deformed
F (dynes)	force, measured on dynamometer beam before spontaneous contraction
f (dynes)	applied stress
σ (dynes per sq. cm.)	actual stress: $\sigma = f(\xi_0 + 1)$
$v_{m(exptl.)}$ (cm. per sec.)	rate of spontaneous contraction from time-displacement graph, recorded by drum of apparatus
$v_{exptl.}$ (cm. per sec.)	rate of spontaneous contraction, extrapolated on zero mass of frame $$v_{exptl.} = \frac{v_{m(exptl.)}}{\sqrt{\frac{M}{M+m}}}$$
v_i (cm. per sec.)	rate of application of impulse: $$v_i = \frac{L_0(\xi_0 + 1)}{\Delta t}$$
ϑ	where Δt = time of complete contraction[1] (see deformation, corresponding to zero value of stress during spontaneous contraction): $$\vartheta = \frac{L_0' - L_0}{l_0}$$
E'_0 (dynes per sq. cm.)	initial modulus of high plasticity[1] $$E_0' = \frac{\sigma}{\xi_0 - \vartheta}$$
v_T (cm. per sec.)	theoretical rate of spontaneous contraction of rubber without friction[1] $$v_T = \sqrt{2[(\xi_0 - \vartheta - \ln(\xi_0 - \vartheta + 1)]} \cdot \sqrt{\frac{E_0'}{\rho}}$$
γ	conventional coefficient of internal friction of rubber $$\gamma = \frac{v_{exptl.}}{v_T}$$
ΔW (kg. per cc.)	specific work of friction $$\Delta W = (1-\gamma^2)[(\xi_0-\vartheta)-\ln(\xi_0-\vartheta+1)]E_0' = (1-\gamma^2)\cdot\frac{\rho v^2 T}{2}$$

of internal friction γ, were also studied. As an example, Table 2 summarizes some results obtained in the testing of Buna S-3 rubber mixtures.

EFFECT OF DEFORMATION

In the present work, the tests of all the rubber mixtures were made at two initial deformations, viz., 100 and 200 per cent. In addition, for Buna S-3 tests were made at 50 and 150 per cent elongation. For all the rubbers studied, an approximately linear relation is observed between the rate of spontaneous contraction and the deformation. For SKB and Buna-S rubbers, the values of the modulus E_0' depended to only a slight extent on the deformation. In this respect, the result clearly agrees with that expected[3]. For natural-rubber mixtures, a certain increase of the modulus E_0' with deformation is observed. In the latter case, the apparent cause of the deviation from linearity is crystallization, which can play a considerable role at room temperature and 200 per cent deformation.[4]

Turning to the data for the relation of the coefficient γ to the deformation, it is necessary to observe that, for unloaded natural-rubber mixtures, no de-

TABLE 2

TEST DATA ON BUNA S-3
(Time of vulcanization 40 minutes)

ρ (g. per cc.)	S (sec.)	L_0 (cm.)	ξ_0	T (° C)	t (min.)	f (kg. per sq. cm.)	σ (kg. per sq. cm.)	ϑ	$\xi_0-\vartheta$	v (cm. per sec.)	V_1 (cm. per sec.)	E_0' (kg. per sq. cm.)	vT (cm. per sec.)	γ	ΔW ergs/cc. $\times 10^6$
0.98	0.98	3.5	1.0	24	5	5.1	10.3	0.35	0.65	2040	6000	15.9	2290	0.93	0.34
					10	4.7	9.5	0.42	0.58	1760	6000	16.3	1890	0.89	0.41
					60	4.4	8.8	0.44	0.56	1700	6000	15.8	1910	0.89	0.37
					180	4.3	8.6	0.46	0.54	1640	5950	15.8	1870	0.88	0.39
					Equil.	4.2	8.5	0.46	0.54	1610	5960	15.9	1830	0.88	0.38
	0.87	3.5	1.0	10	"	4.5	9.0	0.54	0.46	1430	6300	20.8	1850	0.79	0.65
				18	"	4.7	9.5	0.50	0.50	1500	5900	19.0	1900	0.79	0.68
				20	"	4.8	9.6	0.49	0.51	1600	5900	18.8	1920	0.83	0.57
				35	"	5.0	10.0	0.42	0.58	1930	5800	17.2	2080	0.93	0.30
				65	"	5.5	11.0	0.28	0.72	2300	5300	15.3	2360	0.97	0.14
				75	"	5.7	11.4	0.23	0.77	2500	5100	14.9	2540	0.98	0.06

pendence of this factor on the deformation is observed. For SKB and Buna-S rubber mixtures, a tendency of the internal friction to increase with deformation is observed.

EFFECT OF THE TIME THAT THE TEST-SPECIMEN REMAINS DEFORMED

An experimental study of the effect of the time that the specimen is kept stretched on the rate of contraction, $v_{exp.}$ modulus E_0', ϑ, and γ is of particular interest from the point of view of explaining the extent to which the hypotheses developed in the preceding work[1] for the calculation of relaxation correspond to the actual nature of the phenomenon studied.

Proceeding from what has been said earlier[1], it is necessary to consider that the stress relaxation in a deformed specimen must be accompanied by an increase of ϑ, with the value of the initial modulus unchanged. These experiments involve, however, one serious difficulty. This is the fact that spontaneous contraction interrupts the relaxation process at a given deformation. Hence it is necessary, either to carry out tests on a series of parallel specimens, using for each its time in the deformed state, or to operate with one specimen, resorting after each experiment on spontaneous contraction to the repeated stress.

Figure 3-I and 3-II show some results obtained in tests of natural rubber and Buna S-3 by the second method.

It is readily seen that, in complete agreement with the theories developed, the stress relaxation of a deformed rubber mixture is accompanied by a decrease of the rate of spontaneous contraction and an increase of the momentary residual deformation ϑ, whereas it is not related to any changes in the values of the initial modulus E_0' or the coefficient of internal friction γ. The indicated nature of the relation of σ, v, ϑ, E_0, and γ to the time that the test-specimen remains deformed is maintained unchanged for SKB rubber mixtures.

In comparing the values of this characteristic for the various rubbers, a conspicuous difference appears in the values of ϑ (it is clearly necessary to distinguish the values of ϑ for various deformations and times from each other) for natural and synthetic rubbers. Thus, for 100 per cent elongation, for 60 minutes at room temperature, of rubbers vulcanized to their optimum cures, ϑ had the following values: for NK 0.1, for SKB 0.45, and for Buna S-3 0.45.

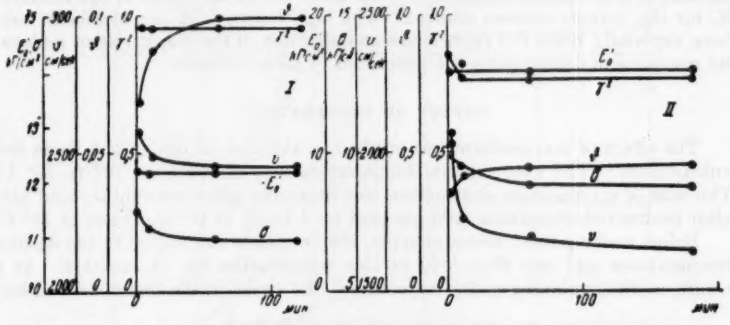


FIG. 3.—σ, E_0', ϑ, v, and γ^3 as functions of the length of time that the test-specimen is held in the deformed state ($\xi_0 = 100\%$). I. Natural rubber (smoked sheet). II. Buna S-3. On the left-hand graph, the ordinates from left to right are E_0' and σ *in kg. per sq. cm.*, v *in cm. per second*, ϑ, and γ^3, respectively; on the right-hand graph, the ordinates from left to right are E_0' *in kg. per sq. cm.*, σ *in kg. per sq. cm.*, v *in cm. per second*, ϑ, and γ^3, respectively. The abscissa in each case is *Time in minutes*.

At sufficiently long times of deformation, ϑ tends toward a certain limiting or equilibrant value, which will henceforth be called ϑ_∞.

Clearly, in this case we have:

$$\sigma_\infty = E_\infty \xi = E_0'(\xi_0 - \vartheta_\infty) \tag{4}$$

for 100 per cent deformation:

$$E_\infty = E_0'(1 - \vartheta_\infty)_{\xi=1} \tag{5}$$

or

$$E_0' - E_\infty = E_1 = E_0' \cdot \vartheta_{\infty,\xi=1} \tag{6}$$

The Equation $E_0' - E_\infty = E_1$, which expresses the nonequilibrium part of the initial modulus of high elasticity, as was explained earlier by Dogadkin, Bartenev, and Reznikovskiĭ[6] and by Dogadkin and Reznikovskiĭ[4], is a very important characteristic of a polymer. However, the lack of a method for determining precisely the initial modulus did not permit these authors to discover the essential differences in the values of E_0' for various polymers.

From the experiments on spontaneous contraction, the value of E_0' can

TABLE 3

VALUES OF THE MODULUS OF HIGH ELASTICITY OF THREE RUBBERS

Type of rubber	$E_1 = E_0' - E_\infty$ at various degrees of vulcanization (minutes)							
	5	10	15	20	25	30	40	60
Buna S-3	6.4	6.4	6.5	6.6	6.1	6.9	6.9	7.0
SKB	—	—	—	—	—	4.5	—	—
Natural rubber	—	—	—	—	—	1.2–2.0	—	—

easily be determined by Equation (6). Such determinations were made for 30-minute vulcanizates of all the rubbers studied. For Buna-S rubbers, besides, the relation of the value of E_1 to the time of vulcanization was studied. The data are given in Table 3.

The absence of a relation between the value of E_1 and the time of vulcanization, as observed in the case of Buna S-3, confirms the correctness of the observations made in earlier work by Dogadkin and Reznikovskil[6]. Quite new and significant is the phenomenon of a sharp difference in the values of the modulus E_1 for the various rubbers studied. The high values of E_1 for synthetic rubbers, especially Buna S-3 rubber, are an indication of the major role of molecular reactions in determining the properties of these rubbers.

EFFECT OF TEMPERATURE

The effect of temperature was studied in the case of one of the Buna S-3 vulcanizates. The experimental temperature was varied from 10° to 75° C. The rate of spontaneous contraction was measured after momentary and also after protracted elongation (100 per cent for 1 hour) or the specimen at 75° C.

Before making these measurements, the specimen was cooled to the desired temperatures and was then held at this temperature for 15 minutes. As a result, at the beginning of the experiment, the stress in the test-specimen had

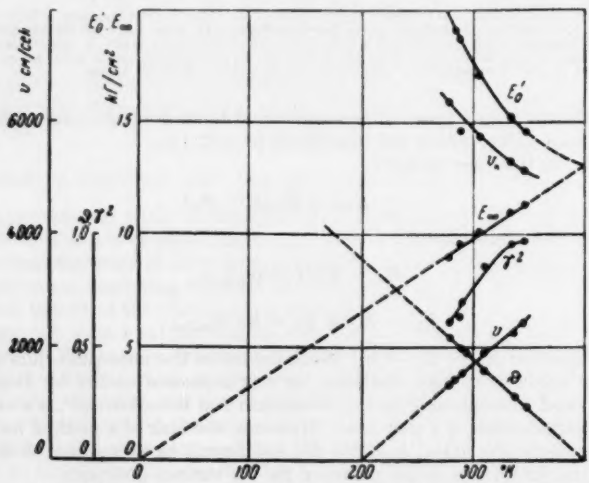


FIG. 4.—v, v_∞, E_∞, E_0', ϑ, and γ^2 as functions of the temperature ($\xi_0 = 100\%$). The three ordinates are, from left to right, v in cm. per sec., ϑ and γ^2, and E_0' and E_∞ in kg. per sq. cm., respectively.

reached practical equilibrium. Figure 4 shows the relation of $\sigma_\infty = E_{\infty\xi=1}$, v, ϑ_∞, E_0', v_i, and γ^2 to the temperature.

From Figure 4 it is seen that the equilibrium modulus E_∞, in accordance with the requirements of the kinetic theory of elasticity, is approximately proportional to the absolute temperature. The rate of spontaneous contraction v in the range studied also increases with rise of temperature, while the initial modulus E_0' and the equilibrium value of the permanent deformation falls with the temperature. The nature of the change of E_0' and ϑ can be understood well, proceeding from the theories of the relation of these parameters to the nature of the intramolecular reaction in the polymer, which is in turn governed by the number and distribution of the secondary van der Waals bonds in the spatial molecular network. According to the experimental data in the graph

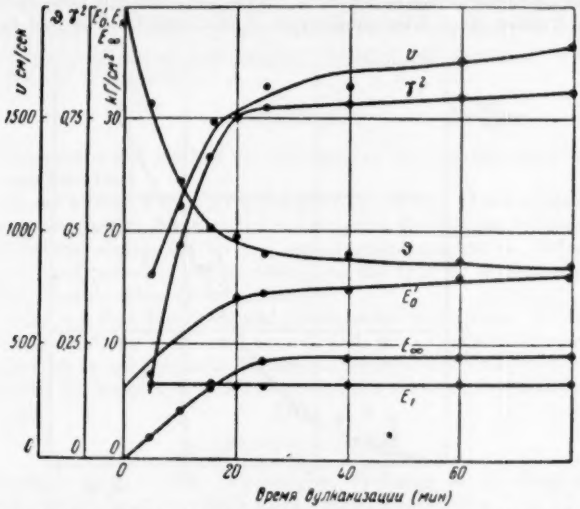


FIG. 5.—The ordinates from left to right are v *in cm. per second*, γ^2, ϑ, and E_0', E_1, and E_∞ *in kg. per sq. cm.*, respectively. The abscissa is (100%). *Time of vulcanization in minutes.* (Buna S-3 rubber).

of Figure 4, the temperature 400° K is critical in the respect that above it (in the absence of chemical changes) the deformation of rubber is not necessarily accompanied by relaxation phenomena ($E_0' - E_\infty \to 0$, $\vartheta_\infty \to 0$).

The increase of the rate of spontaneous contraction with temperature is evidently related, not only to the equilibrium modulus E_∞, but also to the decrease of internal friction. The latter becomes evident in the study of the temperature relation of the coefficient γ^2.

The study of the process of spontaneous contraction at low temperatures may be of great interest from the viewpoint of explaining the mechanism of vitrification. Such a study is a problem to be undertaken later. It may be stated at this point, however, that an approximate extrapolation of the data toward the lower temperatures shows clearly that the rate of spontaneous contraction tends toward a zero value at a temperature near that of vitrification. Since at this temperature the equilibrium modulus does not reach zero, then, in

accord with the basic equation derived in the preceding work[1], either ϑ_∞ approaches unity or the coefficient γ approaches zero. The latter represents physically the unlimited increase of internal friction.

It is interesting that, on the basis of the same rough extrapolation, the value of ϑ in the vitrification region tends toward unity, and this, in accord with Equation (5), denotes an unlimited increase of the part played by the molecular reaction: ($E_0' \to \infty$). Realizing the insufficient reliability of the data obtained by extrapolation, the authors plan to conduct in the future a special study of spontaneous contraction at low temperatures.

EFFECT OF TIME OF VULCANIZATION

The data on the study of the influence of the time of vulcanization for Buna S-3 vulcanizates are shown in Figure 5. As in the preceding case, spontaneous contraction takes place after equilibrium is established. The fact mentioned

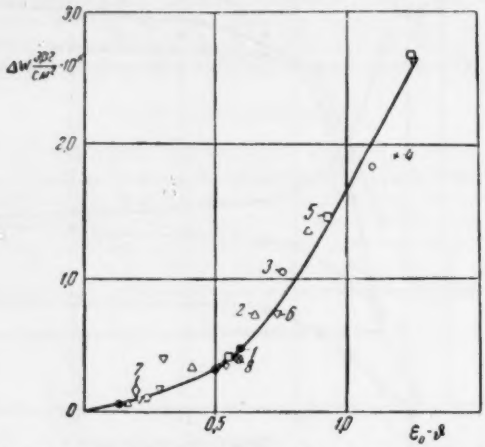


FIG. 6.—Specific work of deformation ΔW as a function of $\xi - \vartheta$. The times of vulcanization on the graph are *1* 5; *2* 10; *3* 15; *4* 20; *5* 25; *6* 40; *7* 60; and *8* 80 minutes. The work, represented by the ordinate, is expressed as ΔW in ergs per sq. cm.

above (Table 3) of the independence of the value of the difference: $E_0' - E_\infty = E_1$, from the time of vulcanization is interesting. The conventional coefficient of internal friction γ changes somewhat during vulcanization, i.e., it increases. According to physical concepts of the coefficient, it is related to the relative hysteresis (ratio of the work of friction to the total work) by the equation:

$$\frac{\Delta W}{W} = 1 - \gamma^2 \tag{7}$$

where ΔW is the specific work of friction and W is the specific work of deformation.

Considering that the specific work of deformation is obtained by the equation:

$$W = [\xi' - \ln(\xi' + 1)]E_0' \tag{8}$$

where $\xi' = \xi_0 - \vartheta$, we obtain for the specific work of friction:

$$\Delta W = (1 - \gamma^2)[\xi' - \ln(\xi' + 1)]E_0' \quad (9)$$

or

$$\Delta W = (1 - \gamma^2)\frac{\rho v_T^2}{2} \quad (10)$$

where v_t is the theoretical rate of contraction (see Table 1).

Figure 6 shows the relation of ΔW to $\xi_0 - \vartheta$ for Buna S-3 vulcanizates as a function of the time of vulcanization. In the construction of the graphs, we used data obtained in the study of spontaneous contraction in relation to the time of vulcanization and the time of deformation.

It is remarkable that all the points on the curve in Figure 6, regardless of the vulcanization time of the corresponding test-specimens and their times of deformation, lie practically on a single curve. This result fully confirms the conclusion made earlier by Dogadkin and Reznikovskiĭ[4] concerning the independence of relaxation properties and internal friction of soft unloaded vulcanizates from the time of vulcanization.

CONCLUSIONS

1. An apparatus and method for the study of the spontaneous contraction of rubber are described.

2. Data are offered which were obtained in a study of the dependence of spontaneous contraction of unloaded vulcanizates of isoprene, butadiene, and butadiene-styrene elastomers on the experimental conditions (deformation, temperature, and period of deformation), on the type of compound, and on technological factors (time of vulcanization).

3. It is shown that the theory of spontaneous contraction of rubber developed by the authors is in good accord with the experimental results, and makes it possible to use the method of spontaneous contraction for determining experimentally the basic factors characterizing the elastic and relaxation properties of rubber.

ACKNOWLEDGMENT

The authors express their gratitude to Professor B. A. Dogadkin and Professor G. M. Bartenev for their comments and assistance.

REFERENCES

[1] Reznikovskiĭ and Khromov, *Kolloid. Zhur.* **14**, 177 (1952).
[2] Mrowca, Dart, and Guth, *J. Applied Physics* **16**, 8 (1945); Rubber Chem. & Technol. **18**, 557 (1945).
[3] Dogadkin, Bartenev, and Reznikovskiĭ, *Kolloid. Zhur.* **11**, 314 (1949); Reznikovskiĭ and Khromov, *Kolloid. Zhur.* **14**, 177 (1952).
[4] Dogadkin and Reznikovskiĭ, *Kolloid. Zhur.* **12**, 102 (1950).
[5] Dogadkin, Bartenev, and Reznikovskii, *Kolloid. Zhur.* **11**, 413 (1949).
[6] Dogadkin and Reznikovskiĭ, *Kolloid. Zhur.* **13**, 11 (1951).

MECHANISM OF THE ACTION OF ACCELERATORS OF VULCANIZATION. VULCANIZATION OF RUBBER BY A SULFUR RADIOISOTOPE *

G. A. Blokh

Kiev Technical Institute of Light Industry, Kiev, USSR

The problem of the mechanism of the action of accelerators and vulcanizing agents during the vulcanization of rubber has been studied in earlier works[1]. It was shown that, during the vulcanization of natural and sodium-butadiene rubber, accelerators of the type of mercaptobenzothiazole and tetramethylthiuram disulfide enter into exchange reactions with the vulcanizing agent, sulfur.

However, the role of the chemically combined sulfur, that is, the so-called bridge sulfur, in the exchange reactions with the accelerators remained unexplained. As Dogadkin and Tarasova[2] show, in the case of sulfur vulcanizates, the following kinds of bonds between the rubber chains can occur:

(1) —C—C—, formed as a result of polymerization or condensation processes (bond energy 62.7 kcal. per mole);

(2) —C—S—C—, monosulfide bonds, formed during thiuram vulcanization (bond energy 54.5 kcal. per mole);

(3) —C—S—S—C—, disulfide bonds;

(4) —C—S_n—C—, polysulfides, formed during vulcanization with elemental sulfur in the absence of accelerators containing sulfur (bond energy 27.5 kcal. per mole).

These authors established the presence of polysulfide bonds by extracting sulfur from vulcanizates, already extracted with cold acetone, by heating the extracted vulcanizate in a 10 per cent solution of sodium sulfite. Ten to twenty per cent of the total amount of combined sulfur was thus extracted as polysulfide, whereas rubber vulcanized with thiuram contained no sulfur at all which could be extracted by sodium sulfite.

In order to study the exchange reactions between accelerators containing sulfur and chemically combined or bridge sulfur, the present investigation was made.

EXPERIMENTAL PART

Vulcanizates of natural and sodium-butadiene rubber were studied. Two per cent of radioactive sulfur (S^{35}) was added to purified pale crepe and sodium-butadiene rubber (SKB). The radioactivity of 1 mg. of the original sulfur was 940 counts per min. The above-mentioned mixtures: pale crepe-sulfur and SKB-sulfur, were vulcanized continuously for 300 minutes at 145° C in a hydraulic press heated electrically. As a result, very thin vulcanized sheets of pale crepe and SKB were obtained, which contained only radioactive sulfur.

* Translated for Rubber Chemistry and Technology from *Doklady Akademii Nauk SSSR*, Vol. 91, No. 5, pages 1107–1110 (1953).

The vulcanization system chosen assured the combination of all of the sulfur with the rubber, i.e., the absence of free sulfur in the vulcanizates[3]. Consequently, in the radioactive-sulfur vulcanizates which were prepared, various types of bonds were present between the rubber chains.

We tested the initial radioactivity of the vulcanized sheets of pale crepe and SKB with special samples. The mean activity of a sample of vulcanized sheet of pale crepe two millimeters thick and diameter equal to that of a "torque" tube (Geiger-Mueller tube or counting tube) was 3368 counts per 10 minutes. The corresponding data for a sample sheet of SKB 0.1 mm. thick was 4110 counts per 10 minutes.

In order to make certain that there was no free radioactive sulfur in the vulcanizates, we extracted them with acetone for 60 hours. The extracts were tested for radioactivity, which was found to be near the background for the counter.

Later, samples, 1.1–1.2 grams by weight, of finely divided vulcanizate were boiled in alcohol and xylene solutions of accelerators (0.2 gram of accelerator dissolved in 20 cc. of solvent). The following accelerators were used in these tests: mercaptobenzothiazole, tetramethylthiuram disulfide, tetramethylthiuram monosulfide, benzothiazylsulfencyclohexylamide, sodium dimethyldithiocarbamate, benzothiazolyl disulfide, and benzothiazylsulfendiethylamide.

The radioactive sulfur vulcanizates were boiled in solutions of alcohol and accelerator for 80 hours, and the xylene-accelerator solutions for 40 hours. After definite periods of time, specimens of accelerator solution, were taken from the reaction system and tested for radioactivity with an end-window counter.

When boiled in xylene-accelerator solutions, the vulcanizates were disintegrated and dissolved. Consequently it was first necessary to separate the vulcanizate from the sample taken; this was done by precipitating it with alcohol, after which the alcohol phase, into which the accelerator had passed, was examined for radioactivity.

If the sulfur which enters into the vulcanizate structure, that is, sulfur which is chemically combined with the rubber, takes part in the exchange reactions with the sulfur of the accelerator, then it is evident that the accelerators will be radioactive, but the radioactivity of the sheets of vulcanizate will decrease after treatment with the solutions of accelerators.

In addition to measuring the radioactivity of the accelerators, the radioactivity of vulcanized sheets was tested after boiling for 60–80 hours in alcohol solutions of accelerators (mercaptobenzothiazole, thiuram, etc.). The mean radioactivity of these sheets was 2793 counts per 10 minutes. The radioactivity of untreated sheets was 2804 counts per 10 minutes. Similar data were obtained for a vulcanizate of SKB, containing 5 per cent of radioactive-combined sulfur, which was heated 9 hours at 145° C. Table 1 shows the results of the measurements of radioactivity of the accelerators.

As is seen from the data in Table 1, the exchange of sulfur atoms under these conditions for the different accelerators varied up to 8.0 per cent (80 hours at 78°), 6.0 per cent (31 hours at 120°), 6.6 per cent (28 hours at 138°).

The small exchange observed can be explained by the fact that a part of the polysulfide bonds in the vulcanizate is destroyed after such a long heat treatment[2], liberating the free sulfur. This free sulfur also takes part in the exchange. The combined sulfur does not take part in the exchange.

In order to study this problem further, it was interesting to study the reactions in a radioactive vulcanizate[4] after it is boiled in a 5–10 per cent solution of sodium sulfite. After this treatment, the vulcanizate should not contain any

TABLE 1

Accelerator	Time of heating (hours)	Heating temperature (° C)	Transfer (%)
Mercaptobenzothiazole	5	78	3.3
	19	78	2.5
	41	78	2.0
	50	78	0.2
	78	78	5.9
	10	138	6.0
	27	138	3.4
Tetramethylthiuram monosulfide	5	78	
	19	78	
	28	78	1.7
	50	78	2.4
	78	78	3.6
	96	78	1.6
	16	138	4.4
Tetramethylthiuram disulfide	10	120	3.0
	25	120	5.0
	31	120	6.0
Sodium dimethyldithiocarbamate	6	100	3.8
	28	100	3.0
Benzothiazylsulfendiethylamide	16	78	3.6
	80	78	8.0
	28	138	6.6

bound polysulfides, and, therefore, exchange of sulfur atoms should not take place. The experiments confirmed this. The results of the radioactivity tests gave: activity of original sulfur, 4000 counts per mg.-min.; activity of sulfur in mercaptobenzothiazole after boiling a radioactive vulcanizate for 2,4, and 10 hours in a xylene solution of mercaptobenzothiazole (the radioactive vulcanizate was first extracted with acetone for 102 hours and treated with a 10 per cent solution of sodium sulfite for 100 hours); 25 counts per mg.-min., was the background count or limit of sensitivity.

Thus, after destruction of the polysulfide bonds, the major part of the cross-linked sulfur, in stable combination in the structure of the vulcanizate, evidently does not take part in the reactions. Further study of this question is of essential importance in the problem of the reclaiming of rubber.

Hence, these experimental data and calculations indicate that, under the technical conditions of rubber vulcanization, as has been shown earlier[1], the free sulfur, not combined with the rubber, takes part in the exchange reactions with the sulfur atoms of the accelerators.

REFERENCES

[1] Blokh, Sazonova, *Zhur. Legk. Prom.* **10** (1952); Blokh, Golubkova, and Miklukhin, *Doklady Akad. Nauk SSSR* **86**, No. 3 (1952); **90**, No. 2 (1953).
[2] Dogadkin and Tarasova, *Doklady Akad. Nauk SSSR* **85**, No. 5 (1952).
[3] Dogadkin, Karmin, and Stukalova, "Physics and Chemistry of Rubbers", M.-L., 1952.
[4] Radioactive vulcanizates were prepared from a natural rubber base and butadiene-styrene copolymer (SKS-30) with the addition of 7 per cent of radioactive sulfur. The recipe also included diphenylguanidine, zinc oxide, and stearic acid. The mixtures were vulcanized at 145° C for 30, 60, 90, and 120 minutes.

THE EFFECT OF MASTERBATCHING, COMPOUNDING, AND TESTING VARIABLES ON CONSTANT-SLIP ABRASION RESULTS *

L. H. HOWLAND, W. W. WHITE, AND W. E. MESSER

SYNTHETIC RUBBER PLANT, NAUGATUCK CHEMICAL DIVISION, NAUGATUCK, CONNECTICUT

PREFACE

It has been reported that a modified Lambourn abrasion test gives results on tire treads which correlate rather well with roadwear data. However, in evaluating tire-tread stocks from carbon black-GR-S masterbatches made in various ways, the results indicated that some machine improvements would be desirable, and that more knowledge of the influence of testing, compounding, and masterbatching variables was required. As a result of this, numerous studies have been made, and these have resulted in considerable knowledge of the problem. Results have been obtained on the effect on abrasion, of such compounding and testing variables as modulus, combined sulfur, the percentage slip, the coefficient of friction of the test wheel, the amount of dusting and type of dust, and ambient temperature.

Test results obtained at various temperatures appear to be of interest in offering a laboratory abrasion test to correlate with roadwear tests performed at different seasons of the year. For testing the temperature variable, an abrasion machine has been built which has a constant-temperature cabinet surrounding the test-wheel and the emery wheel. The improved equipment and techniques resulting from these studies have resulted in the development of masterbatches from oils, carbon black, and high Mooney viscosity cold GR-S that appear to be improvements over previous masterbatches from these respective components.

INTRODUCTION

The constant-slip abrader (modified Lambourn) has been shown by Adams, Reynolds, Messer, and Howland[1] to give reliable laboratory abrasion results which correlate well with road wear in certain testing locations and under certain testing conditions. Although this tool has been of great value, the present program was undertaken for the purpose of refining the machine and the test method, so as to make the results obtained with it still more reliable and more generally applicable as a research tool. The influence of variables in the method itself, such as temperature of testing, talcing rate, and slip of test wheel against the abrasive wheel, have been determined, as well as the effect of variations in composition, compounding, and vulcanization of the test stocks. In addition to these studies on testing and compounding variables, results are shown on the use of the constant-slip abrader in studying the effect of GR-S latex masterbatching variables on the abrasion resistance of tread vulcanizates.

* An original contribution. This paper was presented at the 65th Meeting of the Division of Rubber Chemistry of the American Chemical Society, Louisville, Kentucky, April 14–16, 1954.

PRECISION OF TEST METHOD

The precision of the results obtained at 300 per cent modulus and 1500 lbs. per sq. in. may be judged by the standard deviation of 3.2 per cent which was calculated from results on ten different compounds and vulcanizates of GR-S 1500 compounded with 50 parts of an HAF carbon black. The compounding was performed by two different operators, the vulcanization by four operators, the tensile stress analyses by one operator, and the abrasion testing by two different operators. These results were obtained over a three-month period of testing.

TABLE I

EFFECT OF SULFUR LOADING ON CONSTANT-SLIP ABRASION RESISTANCE

GR-S 1503		100	100	100
Carbon black (HAF)		50	50	50
Zinc oxide		3	3	3
Benzothiazolyl disulfide		0.7	0.7	0.7
Diphenylguanidine		0.3	0.3	0.3
Sulfur		1	1.5	2
Compounded Mooney viscosity (ML-4)		70.5	71.5	72
300% Modulus (lb. per sq. in.) (cured at 292° F)	20′	680	1050	1150
	40′	1140	1870	2240
	60′	1340	1940	2440
	80′	1360	2100	2900
	100′	1380	2120	—
Tensile strength (lb. per sq. in.)	20′	1920	3010	2000
	40′	3080	3210	3020
	60′	3050	3450	2820
	80′	3470	3500	3290
	100′	3380	3720	3020
Elongation (%)	20′	630	580	440
	40′	550	460	400
	60′	(520)	430	360
	80′	550	410	340
	100′	530	440	270
Free Sulfur (%)	20′	0.17	0.18	0.27
	40′	0.07	0.08	0.09
	60′	0.04	0.03	0.03
	80′	0.02	0.02	0.02
	100′	0.02	(0.05)	0.02
Abrasion resistance losses (constant-slip abrader) (cc./3000 feet)	20′	0.386	0.305	0.253
	40′	0.309	0.246	0.225
	60′	0.299	0.251	0.239
	80′	0.280	0.253	(0.204)
	100′	0.276	0.237	0.234

VARIABLES IN TEST METHOD

While using the constant-slip abrader in the evaluation of tread stocks from new materials and from GR-S latex masterbatches prepared by different methods, it became evident that more information was needed concerning the effect of certain variables in the method. At the same time it was found necessary to study the manner in which the results obtained with the abrader were to be interpreted. For instance, the original investigators with this equipment rated stocks at times of cure or states of cure which had been previously selected on the basis of curing characteristics of the stocks. This is satisfactory when the test is being performed in a routine manner on stocks of known behavior, but is

not completely adequate when the equipment and the present known procedure are being used on research vulcanizates. As a result, the studies of the following variables have been made to give an increased amount of knowledge on the subject.

VARIABLE COMBINED SULFUR

Three compounds of GR-S 1503 (a peroxamine activated, fatty acid emulsified, 41° F copolymer) were prepared, containing 50 parts (33.3 per cent) of a high abrasive furnace (HAF) carbon black per 100 parts of polymer, and varying only in the proportion of sulfur added during compounding. The compounding recipe and physical properties of vulcanizates of these compounds are given in Table I. The abrasion loss data are plotted against 300 per cent modulus in Figure 1, where it may be seen that the abrasion loss-300 per cent

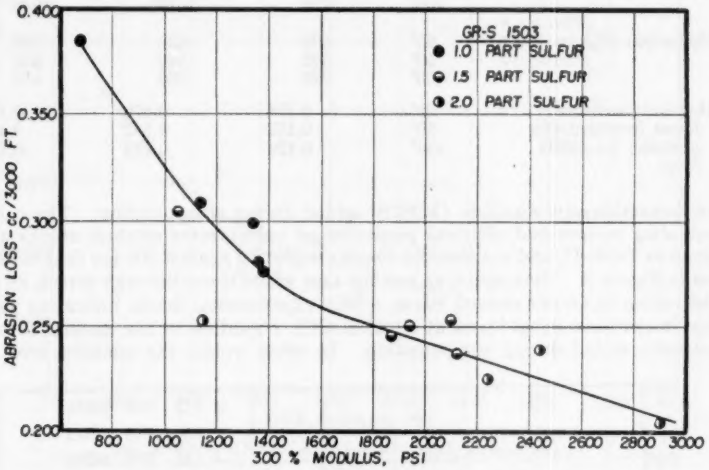


FIG. 1.—Effect of 300% modulus on constant-slip abrasion losses.

modulus values lie on one curve, within experimental limits. This would indicate that the three vulcanizates have equal abrasion losses at equal moduli (equal combined sulfur and, in this case, equal state of cure) and that the losses decrease as the modulus increases. As a result of this, higher abrasion resistances can be obtained with the higher sulfur than the lower sulfur stocks because the latter cannot be cured to so high a modulus as the former.

However, where considerations of service demand a specific modulus value, all comparative stocks must be evaluated at the same modulus, regardless of state of cure.

ACCELERATOR LOADING (RATE OF CURE)

The abrasion loss-300 per cent modulus relationship was also examined by holding the sulfur content constant and varying the amount of accelerator added during compounding. For this study, three compounds of GR-S 1503 were prepared containing 50 parts (33.3 per cent) of an easy processing channel carbon black per 100 parts of polymer and varying only the amount of accelera-

TABLE II

VULCANIZATE PROPERTIES OF STOCKS USED IN STUDY OF EFFECT OF PER CENT SLIP AND ACCELERATOR LEVEL ON CONSTANT SLIP ABRASION LOSSES

GR-S 1503		100	100	100
Carbon black (EPC)		50	50	50
Zinc oxide		5	5	5
Sulfur		2	2	2
Benzothiazolyl disulfide		1.25	1.50	1.75
Compounded Mooney viscosity (ML-4)		88	92	86
300% Modulus (lb. per sq. in.) (cured at 292° F)	25′	908	1200	1100
	50′	1440	1650	1580
	100′	1930	2180	2410
Tensile strength (lb. per sq. in.)	25′	3130	3650	3720
	50′	3580	3950	4050
	100′	3730	3670	3040
Elongation (%)	25′	680	630	700
	50′	570	540	600
	100′	470	430	450
Abrasion resistance losses (constant-slip abrader) (cc./3000 feet)	25′	0.178	0.170	0.160
	50′	0.152	0.142	0.156
	100′	0.129	0.132	0.126

tor benzothiazolyl disulfide (MBTS) added during compounding. The compounding recipes and physical properties of vulcanizates of these stocks are given in Table II, and the abrasion losses are plotted against 300 per cent modulus in Figure 2. Here again, as was the case where the sulfur was varied, all of the values lie on one smooth curve, within experimental limits, indicating that the stocks have equal losses at equal moduli, regardless of the amount of accelerator added during compounding. In other words, the modulus level is

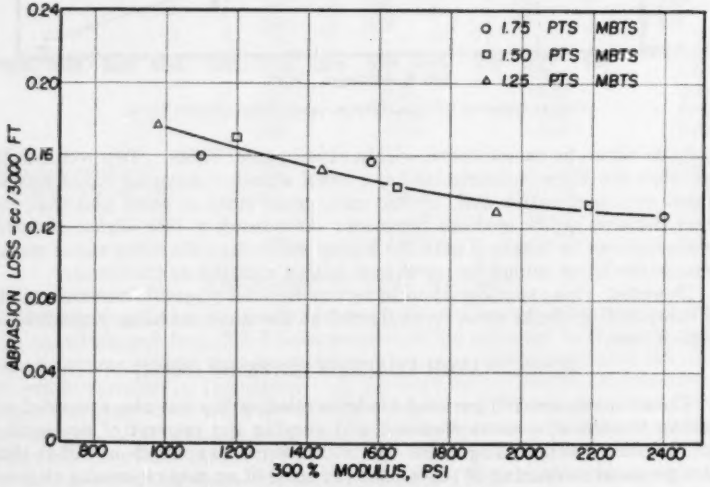


FIG. 2.—Effect of cure level on abrasion loss.

the deciding factor, regardless of the rate of modulus development (rate of cure). This does not appear to be in complete agreement with Adams, Reynolds, Messer, and Howland[1], who felt that a good comparison could not be made by selecting cures at equal modulus for abrasion testing when the cure rates differed considerably. One possible explanation of the apparent failure to obtain as good agreement in the X-571 series of the workers cited as in the MBTS stocks is that two of the X-571 stocks were accelerated with tetramethylthiuram disulfide (Tuex) which is a nonpersistent type of accelerator, in contrast to MBTS, which is regarded as a persistent accelerator. However, when the data for X-571 of Adams, Reynolds, Messer, and Howland are graphed with abrasion loss vs. 300 per cent modulus, as is done in Figure 3, there is some indi-

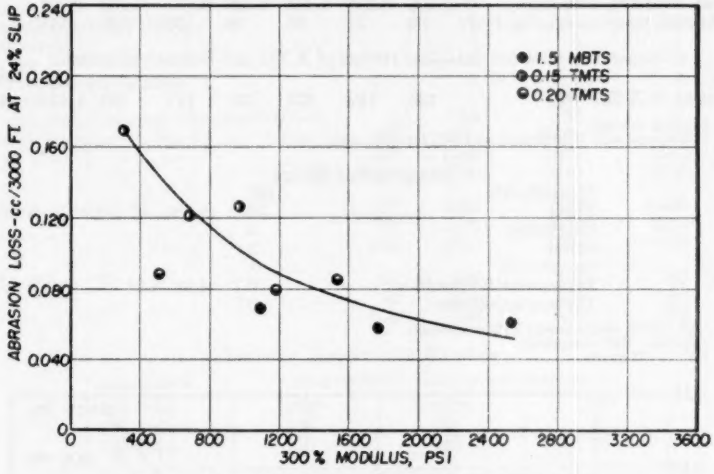


FIG. 3.—Effect of 300% modulus on constant slip abrasion losses.

cation that modulus and abrasion loss do correlate somewhat the same as shown above in the MBTS series.

VARIATION IN COMPOUND—VARIOUS CARBON BLACKS IN DIFFERENT POLYMERS AND MASTERBATCHES

The abrasion loss-300 per cent modulus relationship was studied in vulcanizates of compounds of several different polymers and softener masterbatches, containing 50 parts per 100 parts of polymer or masterbatch, of seven different carbon blacks. One series of compounds was prepared in the laboratory with 25 parts of a naphthenic extender oil in 100 parts of an 111 Mooney viscosity (ML-4) GR-S 1500, and a second series was prepared with the same carbon blacks in X-732 (20 parts of Resin 731 in high Mooney viscosity GR-S 1500). The compounding recipes employed for vulcanizates of these compounds are given in Table III, with the abrasion resistance losses, at 1500 lb. per sq. in.-300 per cent modulus, determined by extrapolation or interpolation on loss vs. 300 per cent modulus curves, for each of the stocks. The abrasion-resistance ratings were calculated with use of the loss for the high abrasion furnace carbon

TABLE III

CONSTANT-SLIP ABRASION RESISTANCE PROPERTIES OF VULCANIZATES OF AN OIL AND A RESIN-731 MASTERBATCH COMPOUNDED WITH VARIOUS CARBON BLACKS

Carbon black type	HMF	GPF	FEF	EPC	HAF	SAF	SAF
Oil Masterbatch (B-2084)							
Abrasion resistance losses (cc./3000 ft. at 1500 lb. per sq. in. 300% modulus)	0.648	0.537	0.361	0.311	0.260	0.170	0.187
Abrasion resistance rating (%)	58	66	84	91	100[a]	120	115
Resin Masterbatch (X-732)							
Abrasion resistance losses (cc./3000 ft. at 1500 lb. per sq. in. 300% modulus)	0.406	0.296	0.206	0.198	0.181	0.153	0.141
Abrasion resistance rating (%)	62	76	93	96	100[a]	108	112
Comparative abrasion resistance ratings of X-732 and B-2084 vulcanizates							*Avg.*
Rating of X-732[b] (%)	123	129	127	122	121	105	114	120

[a] Rating controls.
[b] Compared with B-2048 stock as 100% for each black.

Compounding Recipe

Masterbatch	100		
Black	50		
Zinc oxide	3		
Sulfur	2		
Stearic acid	1		
Benzothiazolyl disulfide	0.7[c]	1.0[c]	1.2[d]
Diphenylguanidine	0.3		

[c] All B-2084 stocks except EPC compound.
[d] B-2084—EPC compound.
[e] All X-732 stocks.

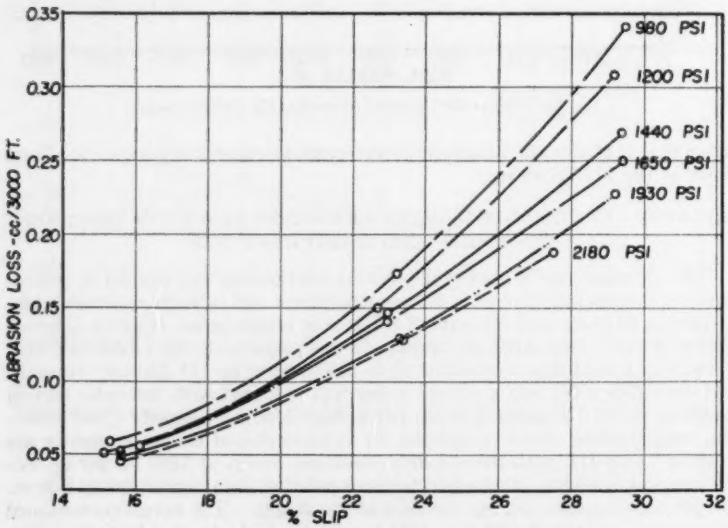


FIG. 4.—Effect of per cent slip on abrasion loss at variable moduli.

black stock as the rating standard. It is evident, by rating these stocks at a given modulus, as has been done here, that the stocks are rated in the order to be expected on the basis of the nature of the black (SAF blacks best—HMF blacks poorest) and that these blacks are rated in the same order in both series. This point is especially significant, since these compounds are at different states of cure when they are compared at equal moduli because of the fact that the different blacks impart different modulus levels at equal states of cure, that

TABLE IV

EFFECT OF VARIABLE TALCING ON CONSTANT SLIP ABRASION RESISTANCE RATINGS

		GR-S 1500	GR-S 1503	J-5181-E
Polymer		100	100	100
Carbon black (EPC)		50	50	50
Zinc oxide		5	5	5
Sulfur		2	2	2
Benzothiazolyl disulfide		1.75	1.75	2
Stearic acid		1	—	1
Compounded Mooney Viscosity (ML-4)		68	86	67
300% Modulus (lb. per sq. in.) (cured at 292° F)	25′	590	1100	750
	50′	1140	1580	1540
	100′	1720	2410	1870
Tensile strength (lb. per sq. in.)	25′	2580	3720	3460
	50′	3640	4650	4360
	100′	3360	4030	4100
Elongation (%)	25′	820	700	780
	50′	660	600	650
	100′	480	450	550

ABRASION RESISTANCE RATINGS

Talcing interval			
	Using 500-foot value for each stock as control		
500 Foot	100*	100*	100*
250 Foot	108	101	87
125 Foot	116	114	95
	Using value for GR-S 1500 at each talcing rate as control		
500 Foot	100*	116	151
250 Foot	100*	110	133
125 Foot	100*	114	134
	Using 500-foot value for GR-S 1500 as control		
500 Foot	100*	116	151
250 Foot	108	118	140
125 Foot	116	129	148

* Rating controls.
All ratings calculated from losses at 1500 lb. per sq. in. —300% modulus obtained by interpolation on loss vs. 300% modulus curves.

is, at equal percentages of combined sulfur. In general, the results in this paper will be reported at 300%-1500 lbs. per sq. in. modulus unless otherwise stated.

It has been shown previously[2] that polymer and carbon black are mutually independent in their effects on tread wear. This point is also evident in the ratings of the stocks from the different masterbatches in the above two series, since the sets of vulcanizates with the same black regardless of the type of black, rate approximately the same. The effect due to the type of masterbatch is shown in Table III, where the relative abrasion resistance rating of the X-732

stocks are compared against the B-2084 stocks containing the same black. These results demonstrate that the resin masterbatch vulcanizates are 20 per cent better in abrasion resistance than the oil masterbatch vulcanizates.

SLIP BETWEEN TEST AND ABRASIVE WHEELS

Another variable which it was felt desirable to investigate further was the effect of the amount of slip between the test and abrasive wheels. In the original procedure it was stated that the slip should be controlled to 24 ± 1 per cent. Two of the three GR-S 1503 vulcanizates which had been used to study the effect of accelerator loading were used for this study. The wheels of each stock at each cure were run at three different slips, with the results shown in Figure 4. The data demonstrate that, as the slip increases, the volume losses increase

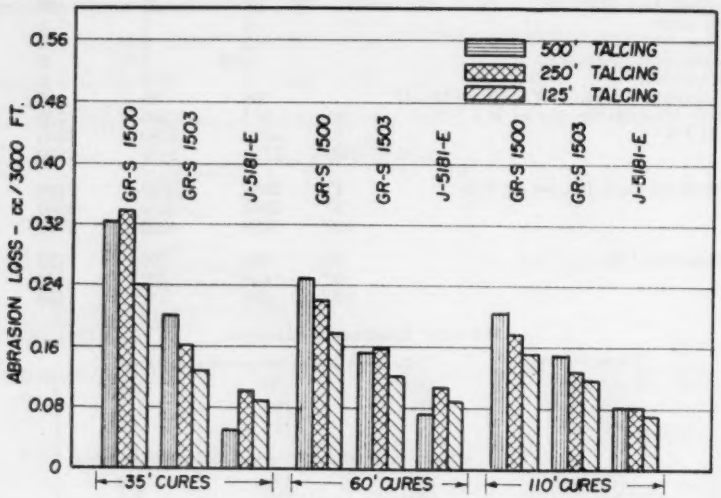


FIG. 5.—Abrasion losses at various talcing rates.

approximately logarithmically. This effect is then, much greater in terms of actual loss for the lower modulus levels, but percentage-wise the effect is fairly constant. It is evident from these data, therefore, that, if reliable results are to be obtained, the slip variation specification of ±1 per cent must be rigidly adhered to and, where possible, should be narrowed.

DUSTING RATE

The procedure as originally set up by Adams, Reynolds, Messer, and Howland[1] specified the application of talc to the test wheel at 500 foot intervals to remove loose abraded material which adhered to the wheel surfaces. However, it has been found, with the advent of resin masterbatches and sometimes with other materials having low modulus, that this talcing rate is not sufficient to keep the wheels free of loose abraded material. In view of this, a series of tests were made at various talcing rates to determine what effect it would have on the abrasion results. For this purpose, tread type compounds of GR-S 1500

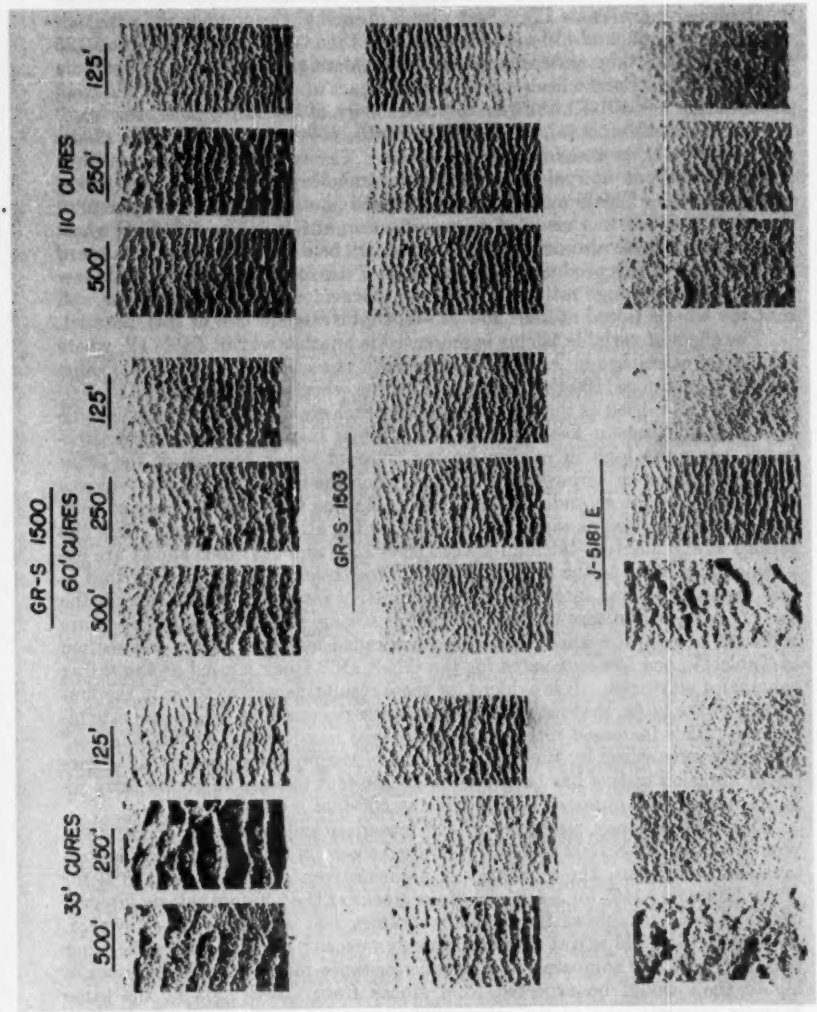


FIG. 6.—Photomicrographs of abraded wheel surfaces at variable talcing.

(sugar-free, rosin-acid emulsified, 41° F butadiene-styrene copolymer), GR-S 1503, and a Resin-731 extended high Mooney viscosity GR-S 1500 (J-5181-E) were prepared. The recipes and unaged stress-strain properties for these stocks are given in Table IV. Test-wheels of each of the compounds were vulcanized for 35, 60, and 110 minutes, and were then talced at 500, 250, and 125 foot intervals as they were abraded on the constant slip abrader. The volume losses of each of these wheels are shown in Figure 5. For all cures of the resin masterbatch (J-5181-E) and the 35-minute cure of the GR-S 1500, the losses are less for the 500-foot talced wheel than for the 250-foot talced wheel. This is different than is the case for the other stocks. The explanation is that, in these cases, the 500-foot interval of talcing was not sufficient to keep the wheels free of loose material. This is evident in the attached photomicrograph (Figure 6) of the wheels, which was made at a magnification of 6×. The J-5181-E wheel surfaces show loose abraded particles which are held on the surface because of the tackiness of this product. The presence of this loose material results in low apparent losses or high ratings. However, it is evident in the photomicrograph that the wheels talced at 250- and 125-foot intervals are free of this material.

The effect of variable talcing is presented in another way in Table IV, where ratings are calculated for each stock. In the first section of this table the value (at 300% modulus-1500 lbs. per sq. in.) for the wheel which was talced at 500-foot intervals is used as the rating control for each stock. It is quite noticeable here that the abrasion losses at 250- and 125-foot talcing, for the resin masterbatch, are quite high in relation to the 500-foot result because of the loose abraded material adhering to the surfaces when the longer talcing interval was employed. In the second section of this table, the GR-S 1500 values at each talcing rate are used as the rating control for the other two stocks. Here the ratings at the 250-foot talcing for the GR-S 1503 and J-5181-E stocks are experimentally equal to the ratings at the 125-foot talcing, and thus show that in this region of talcing intervals, the comparative ratings of stocks remain the same. Also, in the case of these particular stocks, these talcing intervals are sufficient to keep the wheels free of loose abraded material. In the last section of Table IV, the 500-foot value for the GR-S 1500 stock is used as the rating control for all stocks. It is evident for these results, as well as those in the first section of the table, that ratings increase (losses decrease) as the talcing rate increases. This increased rating (decreased loss) is attributed to "lubrication" of the abrasive wheel by the talc. In view of the preceding results, all subsequent abrasion testing has been done with 250-foot talcings to assure more reliable results than obtained with talcing at 500-foot intervals.

Since the Mooney viscosities of the materials and cure rates of the compounds of the GR-S 1500 and J-5181-E stocks used in the talcing study are essentially equivalent, the comparative abrasion resistance ratings (100% for GR-S 1500 and 134% for J-5181-E) of the stocks at the 250-foot talcing interval obtained seem reliable as far as this laboratory test is concerned. However, since the GR-S 1503 was at a higher Mooney viscosity level than were the other two materials, the comparative abrasion resistance rating of its tread stock is higher than would be expected from stocks from GR-S 1503 at the same Mooney viscosity level as the other products, and, hence, is not strictly comparable with results from the other materials.

EVALUATION OF PRODUCTS OTHER THAN TALC FOR REMOVING ABRADED MATERIAL FROM TEST-WHEEL SURFACES

Since the talc used for keeping the wheel surfaces free of abraded material "lubricates" the abrasive wheel to some extent when an excessive amount is

used, a search was initiated for a material which would not have this disadvantage but would still be effective in keeping the wheel free of loose material. Products investigated for this application were zinc oxide, water, Dixie clay, natural ground limestone (Atomite), red iron oxide, and uncompressed HAF carbon black. When zinc oxide or water was used, the wheel surfaces became very tacky, especially with resin masterbatch vulcanizates, and the wheel surfaces had the appearance of having had the polymer melted on the surface. These wheels had smaller volume losses (increased ratings) for the resin masterbatch vulcanizates, and the results were more erratic than when talc was used.

Ground limestone, red iron oxide, and uncompressed HAF carbon black gave results essentially equivalent to those with talc. The wheels dusted with Dixie clay had the highest abrasion losses of any of the wheels tested, and these losses increased as the dusting rate increased. A study of the data from the present investigation indicates that none of these materials offers any advantage over talc as a dusting material in abrasion testing.

COEFFICIENTS OF FRICTION

Another factor which has been found to influence the results obtained by the constant-slip abrasion tester is the coefficient of friction of the test-wheel against the abrasive wheel. During an evaluation of extender masterbatches prepared with extenders containing various components of oils, it was found that a laboratory prepared masterbatch containing 25 parts of paraffin wax in a 125 ML-4 GR-S 1500 gave a tread type vulcanizate which had an abrasion rating of 136 percent, compared with 100 per cent for a similar vulcanizate of X-628. As the abrasion test is now performed, all stocks are abraded at a constant slip of 24 $\pm$ 1 per cent, which is measured by the difference in distances traveled by the test and abrasive wheels. The test wheel is always driven at the same speed and for the same distance, and the slip (percentage difference in the two travel distances) is controlled by applying a braking force to the abrasive wheel to maintain its speed and distance of travel the same in all tests. A test wheel which has a high coefficient of friction tends to drive the abrading wheel faster than one with a low coefficient of friction and, therefore, a greater braking force is needed to maintain the desired speed (slip) of the abrading wheel. This greater braking force results in more severe abrading conditions for stocks of higher coefficients of friction. In other words, if three stocks are equivalent in every respect except their coefficients of friction, that with the highest coefficient of friction should show the lowest abrasion resistance rating and that with the lowest coefficient the highest rating. A simple experiment was run to show that this may be a possible explanation of the high rating for the paraffin-extended vulcanizate. Test wheels were cured 35 minutes and 60 from compounds of the paraffin-wax masterbatch, and X-628 stock, and a Resin-731 masterbatch. These wheels were run on the abrader with the valve on the hydraulic braking system at three different settings. The difference of speed at which the abrasive wheel was driven was a measure of the relative coefficients of friction of the three stocks. The tachometer readings (speeds) are given in Table V. The higher the speed, the higher the coefficient of friction. These data show that the paraffin wax stock has the lowest coefficient of friction, as anticipated, and the rosin masterbatch the highest coefficient of friction. Therefore, it appears that the abrasion resistance rating obtained on the paraffin wax stock may be high compared with what it would be under conditions of equal slip at equal load (measured by the pressure on the oil braking system), whereas the resin masterbatch ratings may be lower than

TABLE V

TACHOMETER READINGS FOR TEST WHEELS OF THREE MASTERBATCH VULCANIZATES

Stock.....		B-2021	B-2024	B-2028
Extender.....		Circosol-2XH	Paraffin Wax	Resin-731
Cure	Valve Opening			
35′	Complete	112	109	115
60′	Complete	112	109	117
35′	One-half turn	96	(60–87)	100
60′	One-half turn	98	(60–87)	103
35′	Closed	28	30	47
60′	Closed	28	28	(42–53)
	COMPOUNDING RECIPE			
Masterbatch		150	100	100
Philblack-O		—	50	50
Zinc oxide		3	3	3
Sulfur		2	2	2
Stearic acid		1	1	1
Benzothiazolyl disulfide		0.7	0.7	1
Diphenylguanidine		0.3	0.2	0.3

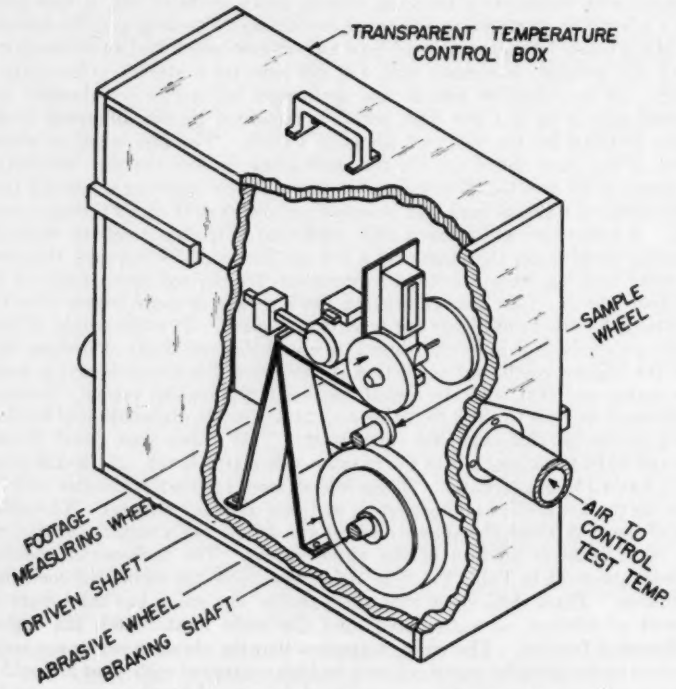


FIG. 7.—Temperature control chamber for constant slip abrader.

would be expected under such conditions. The results suggest that the constant slip abrader should be equipped with some means of determining the actual amount of work done during abrading.

AMBIENT TEMPERATURES

It is well known that the ambient temperature has a marked effect on road wear of tires[2] and that relative road-wear ratings between tire treads made from various rubbers can change with temperature and, in some cases, a product superior at high temperatures may become equal to or inferior at low temperatures[3]. The usual laboratory abrasion test probably correlates best with high temperature or summer operation of tires. It has been felt that, to have a laboratory evaluation method which checks various conditions of tire operation, tests should be run at various temperatures down to the low temperatures experienced in the winter in various regions. For preliminary work, this has been accomplished by placing the constant slip abrader in a constant temperature cabinet. The cabinet was constructed with two sections, connected by two openings placed at opposite ends of the separating partition. A fan was mounted in the section with the abrader to maintain continuous circulation of air. The other section contained a heater, a basket for crushed solid carbon dioxide, and an intermittent fan connected to a thermoregulator mounted in the section close to the test wheel. When tests were made at 30° C or lower, the heater was disconnected, and dry ice was placed in the basket. When the temperature climbed above the set temperature in the test chamber, the thermoregulator activated the intermittent fan and circulated air across the dry ice into the chamber. When the tests were made at 40° C, the basket was removed and the heater was connected to the thermoregulator. With this arrangement, it was possible to maintain the temperature in the chamber within the limits of ±0.5° C of the set temperature.

More recently a machine has been constructed so that the constant-temperature chamber surrounds only the abrasion wheel and test sample. A drawing of this feature of the new machine is shown in Figure 7.

The study of effect of temperature on abrasion was conducted first with vulcanizates of a GR-S 1500 and a Resin-731 masterbatch (J-5181-F) and, later, was extended to cover GR-S 1503 and an oil-extended GR-S 1500 (B-2084) and another pilot-plant Resin-731 masterbatch (J-5181-G). The oil masterbatch (B-2084) was prepared in the laboratory and contained 25 parts of a naphthenic extender oil in a 111 ML-4 GR-S 1500. The compounding formulas and vulcanizate properties of each of these stocks are given in Table VI. The two compounds of GR-S 1500 were prepared from the same bale of GR-S 1500 and the two Resin masterbatches differed in that the J-5181-G was prepared with a latex blend of a high and low Mooney viscosity latex to give the same Mooney viscosity as that used in J-5181-F, which had not been blended. The abrasion losses, at 300 per cent modulus and 1500 lbs. per sq. in. (at 25° C) are plotted against ambient temperature in Figure 8, which shows that the losses for the GR-S 1500, B-2084 and GR-S 1503 vulcanizates increase and the losses for the Resin-731 masterbatch vulcanizate remain essentially constant as the ambient temperature increases from −10° to 30° C. The losses at 40° C are lower than would be expected from the general slopes of the curves, because, at this temperature, the wheel surfaces become tacky and the talc dusting is not efficient in keeping the wheel surfaces free of loose abraded material. There is generally good agreement between the two GR-S 1500 vulcanizates and the two J-5181 vulcanizates (F and G). This is of particular significance

TABLE VI

VULCANIZATE PROPERTIES OF STOCKS USED IN STUDY OF EFFECT OF TEMPERATURE ON ABRASION

		GR-S 1500	GR-S 1500	GR-S 1503	B-2084*	J-5181-F*	J-5181-G
Polymer		100	100	100	100	100	100
Carbon black (HAF)		50	50	50	50	50	50
Zinc oxide		3	3	3	3	3	3
Sulfur		2	2	2	2	2	2
Benzothiazolyl disulfide		0.7	0.7	0.7	0.7	1	1
Diphenylguanidine		0.3	0.3	—	0.3	0.3	0.3
Stearic acid		1	1	—	1	1	1
Compounded Mooney viscosity		74	69	78	65	69	62
300% Modulus (lb. per sq. in.) (cured at 292° F)	25′	800	1210	750	1430	1000	1140
	50′	1870	2220	1450	2130	1780	1960
	100′	2360	2770	2350	2430	2550	2720
Tensile strength (lb. per sq. in.)	25′	1810	2600	1425	2810	2810	2940
	50′	3310	3720	2900	3030	3610	3830
	100′	3640	3800	3610	2970	4120	4140
Elongation (%)	25′	560	580	570	480	650	660
	50′	460	470	510	400	530	510
	100′	430	390	420	350	450	440
Constant-slip abrasion losses (1500 lb. per sq. in.-300% Modulus at 25° C) (cc./3000 ft.)	−10° C	0.118	0.122	0.120	0.166	0.116	0.144
	0° C	0.141	0.135	0.144	0.159	0.141	0.138
	10° C	0.158	0.169	0.187	0.190	0.132	0.138
	20° C	0.207	0.219	0.203	0.227	0.140	0.134
	30° C	0.268	0.249	0.263	0.252	0.141	0.129
	40° C	0.279	0.285	0.311	0.279	(0.097)	0.140

* Compounded as all polymer.

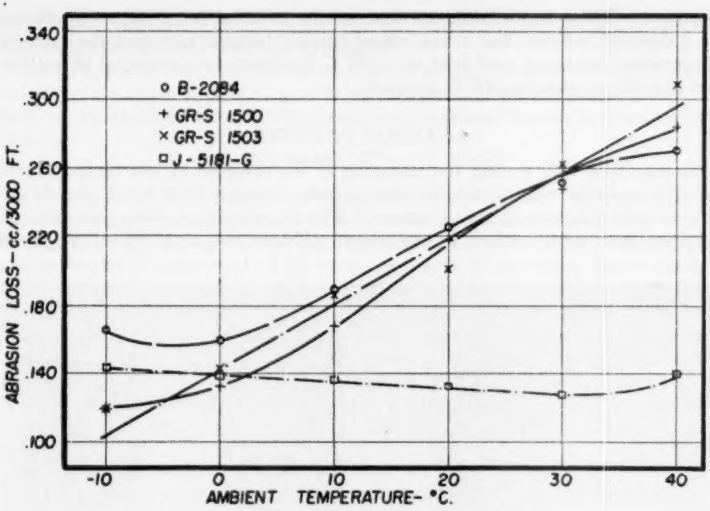


FIG. 8.—Effect of ambient temperature on abrasion loss.

in the case of the two resin masterbatches, since they differed in base polymer content as noted above. Some of these results are not in agreement with the findings of Stiehler, Steel, and Mandel[4] in road-wear tests, for they reported a negative temperature coefficient for cold rubber (X-485) with furnace black. This discrepancy may be due to other seasonal variations affecting the road-wear tests, as pointed out by Stiehler, Steel, and Mandel[3].

Since the constant slip abrasion test is a high-speed test, the wheel surfaces would be expected to be at higher temperatures than the ambient temperatures, so an attempt was made to determine semiquantitatively the temperature of the wheel surfaces after they were abraded at the various ambient temperatures. The wheels were removed immediately after they had been abraded the full 3000 feet, and a copper constantan needle thermocouple was then placed on the wheel surface and the temperature read as soon as the reading was constant. These readings are given in Table VII. The actual magnitude of these readings may be questionable because of the heat capacity of the needle itself as well as the perceptible time lag of reaching constant reading, but they should give an idea of the wheel surface temperatures if compared with ambient tem-

TABLE VII

TEMPERATURES OF CONSTANT-SLIP ABRASION TEST WHEELS AFTER ABRADING

Ambient temperature (° C)	GR-S 1500	GR-S 1503	B-2084	J-5181-G
	Surface temperature (° C)			
−10°	20°	22°	21°	19°
0°	22°	22°	22°	24°
10°	26°	26°	27°	26°
20°	31°	32°	31°	35°
30°	33°	33°	31°	39°
40°	38°	39°	40°	41°

peratures. These results indicate that, as the ambient temperature decreases, the difference between the actual wheel-surface temperature and the ambient temperature increases, and that at −10° C (ambient temperature) this difference may be as great as 30° C or more.

ABRASION PATTERN

It was observed, during the abrading of the samples at low temperatures, that the material was abraded in fine powder instead of in small shreds and rolls, as noted at normal temperatures. The wheel surfaces were also different in appearance, as is evident in the second photomicrograph (12×), Figure 9,

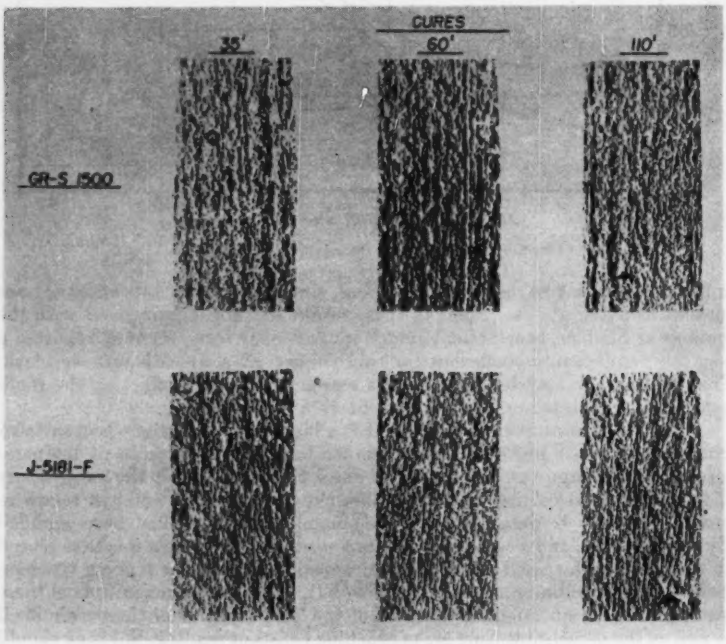


FIG. 9.—Photomicrographs of abraded wheel surfaces. (Ambient temperature −10° C.)

which shows the surfaces of the wheels which were abraded at −10° C. It can be seen here that the abrasion pattern which has been studied by Schallamach[5] and which was apparent in the first photomicrograph, is nonexistent, or at best poorly defined, showing that the nature of the abrasion is different, in degree if not in kind, at low temperatures than it is at high temperatures. The wheels abraded at −10° C have circumferential grooves instead of the parallel ridges at right angles to the plane of the circumference, as evident in the first photomicrograph. These wheel surfaces have the same type of surface that is noticed when a nonrubbery solid is abraded. It is significant that this failure to develop the usual abrasion pattern is evident in spite of the fact that the constant-

slip abrasion test is a high-speed test and the wheel surfaces are above the ambient temperature, as previously illustrated.

It was noted also during the abrasion study at various ambient temperatures that the state of cure, judged by 300 per cent modulus, had considerably less effect on the abrasion losses at the lower temperatures than at higher temperatures.

MASTERBATCHING STUDIES

The results of the study, reported above, of paraffin wax as a possible extender for high Mooney-viscosity GR-S, show how this study of variables in abrasion testing was valuable in limiting the expenditure of time and effort on further studies of a material which would probably be no better than extenders of the oil type in spite of an indication of quality improvements in early tests. This investigation further emphasizes the necessity of evaluating laboratory abrasion results in the light of all known facts before drawing definite conclusions from them. Of course, abrasion testing is not unique in this respect, but since there has been a general reluctance to place confidence in laboratory abrasion tests, it is even more important to evaluate all results more critically so as to prevent the possibility of complete breakdown of confidence in these tests, which do furnish indicative and valuable information.

RESIN MASTERBATCHES

Another example of the use of the abrader in latex masterbatching studies is in the evaluation of resin masterbatches. Constant-slip abrasion resistance results have consistently shown better abrasion resistance for these materials than for regular low-temperature polymers. The results from the coefficient of friction study indicate that these materials may even have better wear resistance than the tests indicate, since they have higher coefficients of friction and therefore work against greater loads than do regular low-temperature polymerized rubbers or oil-extended low-temperature polymers. The superior wearing quality of the resin masterbatches has been shown in a number of road tests on tires with treads made from these materials.

EVALUATION OF SAF (SUPER ABRASION FURNACE) BLACKS

The constant-slip abrasion equipment has proved useful in the evaluation of new materials used in latex masterbatching. Table VIII shows the properties of vulcanized stocks containing an HAF and an SAF black in mill-mixed GR-S 1500 and in oil-black-cold rubber masterbatches prepared with 25 parts of Circosol-2XH in 111 ML-4 GR-S 1500. The constant-slip abrasion resistance results show that the mill-mixed SAF vulcanizate is 21 per cent better than the mill-mixed HAF vulcanizate in this respect, and this is in agreement with the improvement obtained in wear rating for tire treads containing these blacks. Also, the results (135 and 100 per cent, respectively, for the SAF and HAF vulcanizates) for the latex incorporated oil-black masterbatches show that this improvement is obtained in oil-black masterbatches as well and, in fact, indicate that the improvement may be even greater in these stocks.

MASTERBATCHING WITH PREMIXED OIL AND BLACK

The last stock shown in Table VIII was prepared by mixing an aqueous slurry of the carbon black with an emulsion of the oil which had been prepared with a cationic emulsifier. This mixing resulted in an intimate mixture of the oil and carbon black, which was then treated with caustic soda and Marasperse-

CB to make it compatible with the latex to which it was added. The Carbex (mixture of latex and carbon black slurry) was flocculated and dried in the usual manner. The abrasion resistance results for this masterbatch show an improvement (144 compared with 135 per cent) over the oil-black masterbatch prepared in the usual way. This method of masterbatching was developed after studies of methods of latex masterbatching of oil and carbon black had indicated that improved laboratory abrasion resistances were obtained when the oil and carbon black were premixed prior to coprecipitation with the latex. It was found that improvement could be obtained by mixing the oil and black in numerous ways, but the methods which gave the most intimate mixing of the

TABLE VIII

COMPARISON OF HAF AND SAF CARBON BLACKS IN MILL-MIXED AND LATEX-INCORPORATED OIL–BLACK MASTERBATCHES

Masterbatch method		Mill-mixed		Oil-black masterbatches		
		—	—	Regular		Cationic emulsifier
Carbon black		HAF	SAF	HAF	SAF	SAF
Compounded Mooney viscosity, ML-4		72	83	63	66	66
300% Modulus (lb. per sq. in.) (cured at 292° F)	25′	1050	980	1630	1420	530
	50′	1880	1920	2090	2030	1040
	100′	2410	2430	2250	2140	1580
Tensile strength (lb. per sq. in.)	25′	2640	2540	3290	3420	2490
	50′	3530	3750	3180	3740	3780
	100′	3920	3680	3130	3580	3840
Elongation (%)	25′	600	630	540	600	870
	50′	480	490	430	470	660
	100′	430	400	400	430	580
Constant-slip abrasion resistance rating— 1550 lb. per sq. in- 300% Modulus		100*	121	100*	135	144

* Rating control.

two gave the best results. The oil and black were premixed in the following ways in addition to the cationic-anionic procedure:

a. Adding the dry pelletized carbon black to the oil.
b. Adding the oil to the dry carbon black.
c. Atomizing the oil onto the black as it was being agitated.
d. Dissolving the oil in a volatile solvent, mixing this solution with the carbon black and evaporating the solvent.

Aqueous slurries of these oil-black mixtures were prepared with Marasperse-CB as the dispersing agent in the usual manner. These slurries contained large particle, sizes as evidenced by the rapid settling of the oil-black. The oil-black slurries were mixed with the latex, and this mixture flocculated and dried as usual for making carbon black-polymer masterbatches. The use of premixed oil and black has resulted in masterbatches with vulcanizates having 200 to 300 lbs. per sq. in. higher tensile strengths and 12 per cent better abrasion resistance ratings than obtained for a similar masterbatch prepared by the regular method. Since indications are that the best results are obtained with intimate mixtures

of oil and black, this can probably be done in the carbon-black producing plants before pelletizing of the black. This improvement in quality has been obtained with paraffinic oils (Necton-60) and with aromatic oils (Dutrex-20 and Process Oil No. 1) as well as with the naphthenic oil (Circosol-2XH). This improvement by oil-coating has also been obtained with SAF blacks.

SUMMARY

A study of factors which affect the results obtained with the constant slip abrader in evaluation of abrasion resistance properties of GR-S vulcanizates has revealed the following:

1. As might be expected, abrasion losses decrease with increase in 300 per cent modulus.
2. Losses increase approximately logarithmically as the amount of slip between the test and abrasive wheels increases.
3. The abrasion losses decrease with increase in talcing rate, due to "lubrication" of the abrasive wheel by the talc as long as the rate is sufficient to keep the wheel free of loose abraded material.
4. Indications are that abrasion losses may increase with increase of coefficients of friction of test wheels against the abrasion wheel.
5. In a study of the effect of ambient temperature on constant slip abrasion losses, the losses increased as the temperature was raised from −10 to 30° C for GR-S 1500, GR-S 1503, and for high Mooney-viscosity GR-S 1500 extended with a naphthenic extender oil, and the losses remained essentially constant for the Resin-731 extended high Mooney viscosity GR-S 1500. The Resin-731 extended stock changed only slightly with temperature and, consequently, its comparative rating increased rapidly with rise of temperature. It was noted in photomicrographs of the wheel surfaces that the abrasion pattern which was evident at normal temperatures was absent or at best poorly defined at the lower temperatures, indicating a possible difference in kind of abrasion at low temperatures than at normal temperatures.
6. Latex masterbatches of oil and black that had been premixed by several different methods gave vulcanizates with constant-slip abrasion resistance superior to similar masterbatches prepared in the usual manner.
7. The constant-slip abrader was found to be useful in evaluating new SAF blacks and in the evaluation of the effect of using dispersing agents in carbon black and extender-carbon black masterbatching by the latex procedure.

ACKNOWLEDGMENT

This work was carried out under the sponsorship of the Office of Synthetic Rubber of the Federal Facilities Corporation, in connection with the Government's synthetic rubber program.

The authors wish to thank that agency for permission to release this publication. The assistance of J. A. Reynolds, who aided in the photomicrographic work and chart preparation, and the assistance of the physical testing laboratory personnel, is appreciated.

REFERENCES

[1] Adams, Reynolds, Messer, and Howland, RUBBER CHEM. & TECHNOL. 25, 191 (1952).
[2] Stiehler, Steel, and Mandel, *Trans. Inst. Rubber Ind.* 27, 298 (1951): RUBBER CHEM. & TECHNOL. 25, 656 (1952); Sjothun, Greer, and Rhodes, *Rubber Age* (N. Y.) 74, 231 (1953).
[3] Sjothun, Greer, and Rhodes, *Rubber Age* (N. Y.) 74, 231 (1953).
[4] Stiehler, Steel, and Mandel, *Trans. Inst. Rubber Ind.* 27, 298 (1951); RUBBER CHEM. & TECHNOL. 25, 656 (1952).
[5] Schallamach, *Trans. Inst. Rubber Ind.* 28, 256 (1952); RUBBER CHEM. & TECHNOL. 26, 230 (1953).

AIR PERMEABILITY OF ELASTOMERS BY DIFFUSION TESTS *

M. CZUHA

GOVERNMENT LABORATORIES, UNIVERSITY OF AKRON, AKRON, OHIO

The various techniques developed for the measurement of the permeability of elastomers to gases involve either absorption[1] or flow measurement[2]. A manometric flow method developed by the B. F. Goodrich Co.[3] utilizes a modified Warburg apparatus[4] commonly used in biological studies to measure small amounts of gases evolved and absorbed by tissues. The apparatus was modified by replacing the respiration flasks with diffusion cells. The direct measurement of the amount of gas passing through a polymer specimen of convenient size and thickness in a relatively short time makes this technique attractive from the standpoint of simplicity of operation. Since few data have been reported in the literature on loaded stocks, the purpose of this study was to examine the merits of this test when applied to vulcanizates of the tire-tread type.

EQUIPMENT AND PROCEDURE

The diffusion apparatus is a modified Warburg unit (Figure 1), in which the respiration flasks are replaced by diffusion cells connected to a gas manifold. Six diffusion cells (Figure 2), each connected to a manometer, are immersed in a water bath, the temperature of which is usually maintained at 30 ± 0.1° C. The rate of diffusion is observed as the displacement of liquid in the arm of the manometer connected to the downstream side of the diffusion cell and separated from the gas under pressure by the polymer. A 60-psi. pressure gauge is used to measure the pressure of the gas in the manifold; the pressure applied in the test is 48 psi. A leveling device makes possible manometer readings at atmospheric pressure, indicated by a standard mercurial barometer. The temperature of the room is maintained at 25° C. The liquid (Brodie solution) in the manometer is an aqueous salt solution (density 1.028) containing a red dye. The manometer factor (approximately 2 cu. mm. per mm. of displacement) is determined for each manometer by weighing the mercury that is found to occupy a measured length of capillary in the manometer.

The diffusion cell is constructed of two circular, recessed stainless-steel plates, between which the test-piece is clamped. A porous Alundum disk on one side of the cell serves as a support for the polymer specimen. The connection between the cell and the manometer is a stainless-steel capillary tube, with an internal diameter of approximately 0.025 inch. The coupling is filled with lead and drilled to reduce the downstream volume, which is approximately two cc. The total volume of gas diffusing through the cell during the test is of the order of one cc. The dimensions of the diffusion region within the polymer are 12.57 square-inch area and 0.025 inch thickness; the average thickness is

* Reprinted from the *India Rubber World*, Vol. 130, No. 2, pages 207–210, May 1954. The work was performed as a part of the research project sponsored by the Office of Synthetic Rubber, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program.

obtained by gauging the polymer at five positions, using a Randall and Stickney gauge.

An equilibration period of three hours after loading is required to reach a steady rate of diffusion, at which time the rate of diffusion is measured every five minutes for 30 minutes. A repeat test is then conducted for an additional 30 minutes, and the amounts of gas diffused during both periods are added to

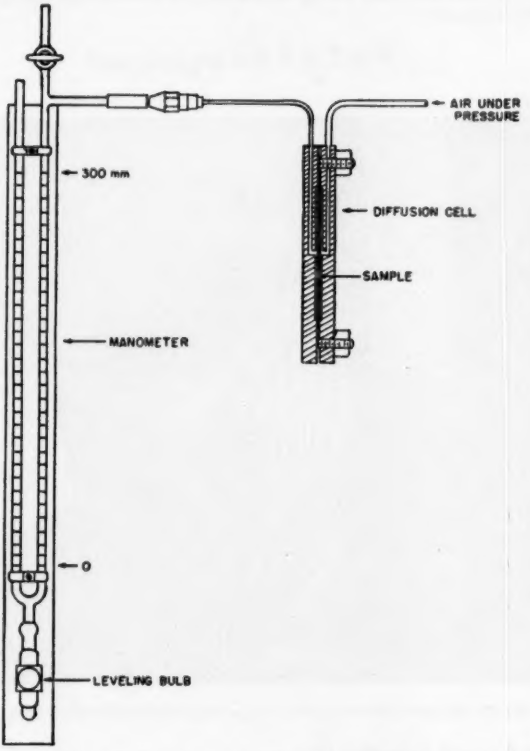


FIG. 1.—Schematic drawing of modified Warburg diffusion apparatus.

give the total manometer reading in cc. per hour. In general, the agreement between the two 30-minute readings was 1 per cent or less.

The permeation coefficient or permeability, Q, at steady state diffusion[4] is given by the equation:

$$q = \frac{Q\,A \times t(p_1 - p_2)}{d} \tag{1}$$

By rearrangement:

$$Q = \frac{qd}{A \times t(p_1 - p_2)} \tag{2}$$

where q = volume of gas diffusing through polymer.
d = thickness of the polymer specimen.
A = area of the polymer surface.
t = time of diffusion.
p_1 = pressure on the surface of the polymer incident to the diffusing gas.
p_2 = pressure on the downstream surface of the polymer.

In terms of data collected in the laboratory, Equation (2) can be rewritten in the units as shown:

$$Q = \frac{M \times F \times B \times d}{P} \times 2.97 \times 10^{-7} \qquad (3)$$

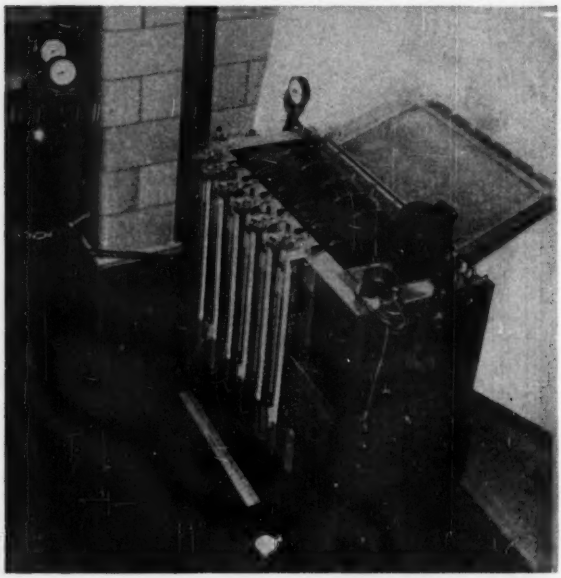


FIG. 2.—Six-unit diffusion apparatus in controlled temperature water bath.

where M $\times$ F = q in Equation (2)

M = manometer reading, mm. per hr.
F = factor for converting unit manometer readings to cc.
d = thickness of the polymer in thousandths of an inch.
P = $(p_1 - p_2)$ in Equation (2), is the pressure drop across the polymer, psi.
B = atmospheric pressure, in mm. of Hg.

The factor 2.97×10^{-7} times B includes the following conversion factors: the volume of the gas from cc. to cu. ft., the area of the disk from sq. in. to sq. ft., the time from hours to days, and corrects the volume of gas to standard conditions of temperature and pressure (32° F and 29.92 in. Hg).

Permeability is thus defined as the number of cubic feet of air (at 32° F and 29.92 in. Hg) diffusing through 0.001 inch thickness of polymer under a pressure differential of one psi. per sq. ft. of polymer per day.

ACCURACY AND REPRODUCIBILITY

The accuracy of the measurements in absolute units was unceratin, since no other test was available for checking the results. However, the present values

TABLE 1

POLYMER TYPES AND COMPOUNDS USED

		Compounding recipe
1.	Natural rubber	A
2.	GR-I	B
3.§	X-603, 71.5/28.5 BD/S	C
4.	23HPA Bld, 72/28 BD/S, high-gel copolymer prepared at 122° F	C
5.	GR-S-1008, 72/27.5/0 BD/S/DVB prepared at 124–127° F	F
6.	X-672, 75/25 BD/S, prepared at 41° F	D
7.	40HK3–6 Bld, 75/25 BD/S, prepared at 41° F	E
8.	¶XP-225, 75/25 BD/S, prepared at 41° F, and masterbatched with 45 parts Circosol-2XH	I
9.	XP-226, 75/25 BD/S, prepared at 41° F, and masterbatched with 45 parts Dutrex-20	I
10.	XP-169, polybutadiene prepared at 14° F	D
11.	IZ Bld 20, polybutadiene prepared at 122° F	D
12.	XP-193, 95/5 BD/S prepared at 122° F	D
13.	XP-203, 85/15 BD/S prepared at 122° F	C
14.	XP-205, 90/10 BD/S prepared at 14° F	D
15.	XP-204, 75/25 BD/S prepared at 14° F	D
16.	78PC29 Bld 2, 75/25 BD/S sodium-catalyzed	H
17.	60E18 Bld 32, 75/25 BD/S Alfin	G
18.	60E18 Bld 33, 75/25 BD/S Alfin	G

COMPOUNDING RECIPES

	A	B	C	D	E	F	G	H	I
Polymer	100	100	100	100	100	100	100	100	100
Oil	—	—	—	—	—	—	—	—	45
EPC black	40	50	40	*40	40	40	40	40	72.5
Zinc oxide	5	5	5	5	5	5	5	5	5
Sulfur	3	2	2	2	2	2	1.5	2	2.64
Altax†	—	0.5	1.75	3	2.35	2	2.25	1.25	3
Captax†	0.5	—	—	—	—	—	—	—	—
Methyl tuads†	—	1	—	—	—	—	—	—	—
Stearic acid	3	3	—	1.5	0.75	1.5	—	3	1.5
PBNA‡	1.5	—	—	—	—	—	—	—	—

* 10, 20, and 60 parts were also used in the study of the effect of carbon black (X-672).
† R. T. Vanderbilt Co., New York, N. Y.
‡ Phenyl-beta-naphthylamine.
§ Sun Oil Co., Philadelphia, Pa.
¶ Shell Oil Co., New York.

reported for the permeability of natural-rubber compounds are in good agreement with those for natural-gum vulcanizates determined by others,[7,8] when allowance is made for the effects of carbon black loading and variations of cure.

The reproducibility of the air-diffusion tests was determined on a standard control copolymer, 41°F GR-S-1500, 75/25 BD/S (X-672). The average of 20 measurements was 3.4×10^{-3} with an average deviation of 0.06×10^{-3}. The values ranged from 3.3 to 3.6×10^{-3}. The determination of the thickness

of the polymer was the least accurate part of the diffusion test. Although it was possible to measure the thickness at any given point to 0.001 inch, it was difficult to cure disks of uniform thickness at every point, and variations as high as 0.006 inch occurred across the disk.

TYPICAL RESULTS

Table 1 lists some of the polymer types and compounding recipes used in this study. The specimens were cured 10 to 15 minutes longer than the optimum cure, selected on the basis of the 300 per cent modulus values, except where measurements over a range of cures were desired. All the compounds were cured at 292° F, with the exception of natural rubber and Butyl compounds, cured at 280 and 307° F, respectively.

Stress-strain tests were conducted in accordance with the standard procedure of the Office of Synthetic Rubber.

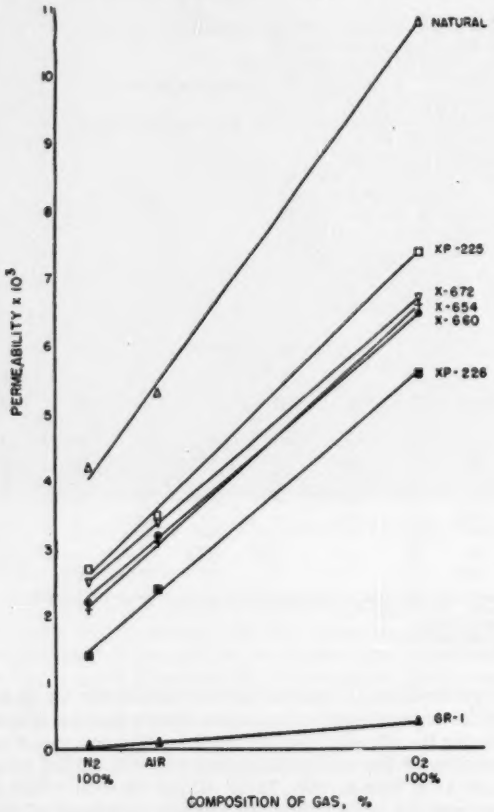


FIG. 3.—Permeability of several polymers to various gases.

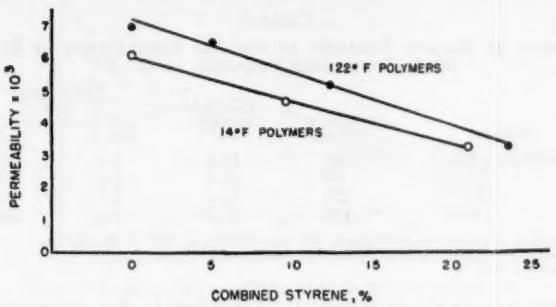


FIG. 4.—Effect of styrene content and polymerization temperature of BD/S copolymers on air permeability.

GAS COMPOSITION

Figure 3 shows the permeability of several polymers as a function of the gas composition. The permeability to nitrogen, air, and oxygen of 75/25 BD/S copolymers (XP-225 and XP-226) prepared at 41° F and masterbatched with two types of processing oil is compared with values for non-oil X-672, natural rubber, and GR-I. The linear relation of the data indicates that the permeability of a polymer is an additive property for a mixture of gases. The greater permeability of a given polymer to oxygen than to nitrogen is attributed to the smaller molecular diameter and greater solubility of oxygen in the polymer[8]. The nature of the processing oil also has some effect on the permeability. Circosol-2XH appeared to increase slightly the permeability of copolymer prepared at 41°F, even with the increased carbon black loading (XP-225). Masterbatching with Dutrex-20 decreased the permeability of copolymer prepared at 41°F(XP-226). Although the permeability is affected to a slight degree by the nature of the oil, the change is insignificant when compared to the variation with polymer type; the GR-S type polymers have a lower permeability than has natural rubber, but higher than GR-I polymer.

POLYMER COMPOSITION AND STRUCTURE

The effects of composition and structure on the permeability of the polymer, as evidenced by results of the effects of combined styrene and polymerization

TABLE 2

EFFECT OF STYRENE CONTENT ON AIR PERMEABILITY

Polymers	Compounding recipe	Combined styrene* (%)	Time of cure at 292° F min.	Permeability† $\times 10^3$
Polybutadiene (1Z Bld 20), 122° F	D	Nil	60	7.0
95/5 BD/S (XP-193), 122° F	D	5.0	45	6.5
85/15 BD/S (XP-203), 122° F	C	12.4	50	5.2
(X-603) 71.5/28.5 BD/S 122° F	C	23.5	55	3.3
Polybutadiene (XP-169), 14° F	D	Nil	45	6.1
90/10 BD/S (XP-205), 14° F	D	9.6	50	4.7
75/25 BD/S (XP-204), 14° F	D	21.0	50	3.3

* By the refractive index method.
† Cubic foot of air (at 32° F and 29.92 in. Hg) diffusing through 0.001 inch thickness of polymer under a pressure differential of one psi. per square foot of polymer per day.

TABLE 3

EFFECT OF MOONEY VISCOSITY ON THE AIR PERMEABILITY OF 75/25 BD/S COPOLYMERS PREPARED AT 41° F*

Polymers	Viscosity ML-4	Combined styrene† (%)	Permeability‡ ×10⁸ Test A	Test B
40HK3-6 Bld.	61	19.3	3.6	3.7
7F1-M	90	19.7	3.6	3.6
5F2-M	120	19.1	3.5	3.5
1F2-M	150	21.7	3.5	3.8

* Compounding recipe E used throughout, with time of cure at 292° F, 50 minutes.
† By refractometer calibrated for 122° F GR-S copolymers.
‡ See footnote†, Table 2.

temperature, are shown in Figure 4. According to the corresponding data presented in Table 2, an increase of 10 per cent in combined styrene resulted in a 23 to 36 per cent decrease of permeability. The permeability was less for polymers prepared at low temperature than for those at high temperature. This effect was greatest for polybutadiene and copolymers of low combined-styrene

TABLE 4

EFFECT OF GEL CONTENT AND DSV ON THE PERMEABILITY OF POLYMERS

Polymer	BD/S/DVB	Gel (%)	DSV	Compounding recipe	Combined styrene (%)	Time of cure at 292° F (min.)	Permeability‡ ×10⁸
X-603	71.5/28.5/0	3	2.21	C	23.5	55	3.3
23HPA Bld. (122° F)	72/28/0	65	0.75	C	27.6	45	3.1
GR-S-1008	72/27.5/0.5	81	0.55	F	22.9	50	3.4

‡ See footnote†, Table 2.

contents. Apparently a polymer structural influence on permeability, dependent on the temperature of polymerization, resides in the butadiene part of the polymer molecule.

MOONEY VISCOSITY

The effect of Mooney viscosity of the base polymer on the permeability of the vulcanizate was investigated, over the range of 61 to 150 ML-4, for a GR-S-

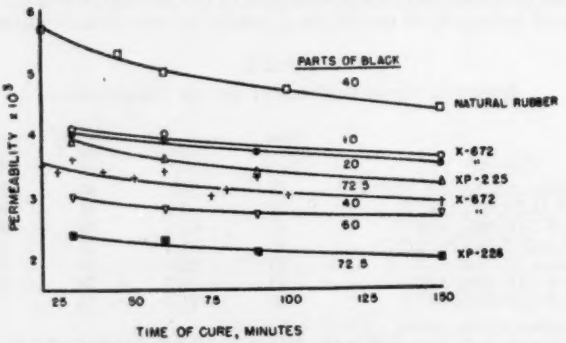


FIG. 5.—Variation of air permeability with time of cure and carbon black content for several polymers.

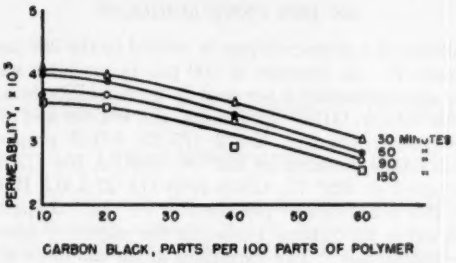


FIG. 6.—Variation of air permeability of 41° F BD/S copolymer with black content at various cures.

1500 75/25 BD/S copolymer. Tests A and B were made on duplicate samples of compounds containing 40 parts of EPC black and cured for 50 minutes at 292° F. The results in Table 3 indicate that there is no significant variation of permeability with ML-4 viscosity of the base polymers.

GEL CONTENT AND DSV

The gel content and dilute solution viscosity of the base polymers appear to have no relation to the permeability of X-603, GR-S, and GR-S-1008 vulcanizates. The data in Table 4 show a slight variation in permeability which probably is the result of differences in combined styrene content.

CURE AND CARBON BLACK

Figures 5 and 6 show an almost linear dependence of permeability on time of cure and carbon black loading. The curing time was varied from 30 to 150 minutes for natural rubber, X-672, XP-225, and for XP-226.

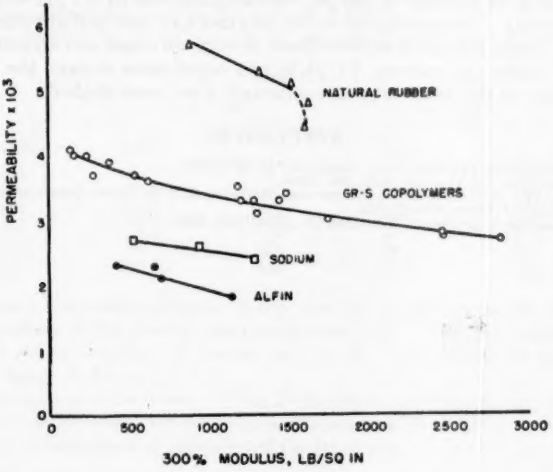


FIG. 7.—Variation of air permeability with 300 per cent modulus for natural and different synthetic rubbers.

300 PER CENT MODULUS

The permeability of a given polymer is related to the 300 per cent modulus as shown in Figure 7. An increase of 100 psi. in modulus was accompanied by a decrease of approximately 2 per cent in permeability to air. Curves are shown for natural rubber, GR-S copolymers, and sodium and alfin copolymers. The GR-S copolymers included X-672 (75/25 BD/S prepared at 41° F), X-603 (71.5/28.5 BD/S prepared at 122° F), 23HPA Bld (72/28 BD/S, high-gel polymer prepared at 122° F), GR-S-1008 (72/27.5/0.5 BD/S/DVB), and XP-204 (75/25 BD/S copolymer prepared at 14° F). Apparently there is a reversion in the curve for natural rubber in the region of overcure, shown in Figure 7 by the dotted line. The variations of the modulus of natural rubber and sodium and alfin polymers were obtained by varying the time of cure. The extended range in modulus for the GR-S copolymers was effected by varying both the time of cure and carbon black loading of X-672.

SUMMARY AND CONCLUSIONS

The permeability of various tread compounds to air was measured in a modified Warburg diffusion apparatus. Measurements were made at 30° C, with air applied at 48 psi. pressure, on molded disks approximately 0.025 inch thick and an area of 12.57 sq. in. The tests were reproducible within 4 per cent on control specimens. The compounds investigated showed permeabilities intermediate between the low values for Butyl and the high values for natural rubber.

The permeability decreased with increasing combined styrene contents and with a decrease of temperature of polymerization for polybutadiene and low-styrene copolymers. It was unaffected by variation over a large range in polymer Mooney viscosity, gel content, and dilute-solution viscosity.

A slight and almost linear decrease of permeability was found with increases in time of cure and carbon black loading for the stocks. In terms of the 300 per cent modulus, an increase of 100 psi. was accompanied by a 2 per cent decrease in permeability. Processing oil in the polymer had only a slight effect on permeability, when compared to the effects of compositional and structural modifications. Alfin and sodium, 75/25 BD/S, copolymers showed the lowest air permeability of the tread type of compounds that were studied.

REFERENCES

[1] Carpenter and Twiss, *Ind. Eng. Chem.* (Anal. Ed.) **12**, 99 (1940).
[2] Daynes, *Proc. Roy. Soc.* (London) **A97**, 286 (1920).
[3] Carpenter, A. W., B. F. Goodrich Co., private communication to B. G. Labbe, Government Laboratories, University of Akron, Feb. 6, 1952.
[4] Dixon, "Manometric Methods", Macmillan Co., New York, 1934.

THE PLASTICIZATION OF RUBBER ON ROLL MILLS *

EUGENE STALINSKY

Consider two mills with rolls of the same diameter, and assume that the rolls rotate n and n', respectively, turns per minute, between 12 and 30. Let t and t' be the times in minutes necessary to bring the same standard amount of rubber to the same degree of plasticity on each mill.

It can be shown experimentally that the times t and t', expressed in minutes, are related in the following way:

$$n \cdot t = n' \cdot t' = N \tag{1}$$

whence:

$$t = N/n \quad \text{and} \quad t' = N/n$$

It follows that the time of plasticization varies in inverse ratio to the speed of the front rolls.

TABLE 1

Length (mm.)	Diameter (mm.)	Speed of front rolls (turns per min. n)
1300	500	12.42
1300	500	17.37

Moreover, the product $n \cdot t$, representing the total number of rotations N that the front roll must make to bring the rubber to a given plasticity p depends only on this value.

Plasticization tests were made on two industrial mills, the rolls of which had the characteristics shown in the following Table 1.

Natural rubber (No. 2 smoked sheet) was plasticized on each mill; in each

TABLE 2

	n = 17.37		n' = 12.42	
Williams plasticity	t (min.)	N	t' (min.)	N
5.8	—	—	12.5	156
5.4	9.5	165	14	174
5.0	12.5	216	17.5	218
4.6	15.5	270	22	275
4.2	19	330	28	350
3.8	23	400	34.5	430

case an amount corresponding to 19 dm^3 per m^2. of surface of the front roll. The temperature of the rubber was maintained at 60° C during plasticization.

Table 2 shows the t and t' values and the $N = n \cdot t$ values for plasticities within the range of 5.8 to 3.8.

An examination of the data in Table 2 will show that the number of turns N necessary to plasticize the rubber from a Williams value of 5.8 to a value of 3.8 is practically independent of the speed of the front roll.

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Revue Générale du Caoutchouc*, No. 3, page 216, March 1954.

It was further established that the relation between p and N is of the form:

$$p = K\sqrt{N} + p_0$$

In this equation, p_0 represents the plasticity attained for very high values of N. K is a constant.

The values of the constants were derived from the numerical data in Table 2. They were found to be: $p_0 = 0.8$ and $K = 60$. The maximum deviations of the K values ranged from -2 to $+4$.

In conclusion, the work shows that it is possible to determine, for a mill whose front roll has a speed of n turns per minute, the time required to plasticize a given weight of any elastomer of homogeneous composition to any predetermined degree of plasticity.

CHOICE OF SOLVENT FOR THE VISCOMETRIC DETERMINATION OF MOLECULAR WEIGHTS OF HIGH POLYMERS *

L. H. CRAGG, R. H. SONES, AND T. E. DUMITRU

DEPARTMENT OF CHEMISTRY, HAMILTON COLLEGE, MCMASTER UNIVERSITY, HAMILTON, ONTARIO, CANADA

The most convenient and, therefore, the most widely used method of determining the molecular weight of a high polymer involves the use of the empirical equation[1]:

$$[\eta] = KM^a \tag{1}$$

in which $[\eta]$ is the intrinsic viscosity, M the molecular weight (or, better, the viscosity-average molecular weight[2], since all polymer samples are more or less heterogeneous with respect to molecular weight), and K and a are empirical "constants". For a given polymer, values of K and a may be obtained from suitable calibration experiments with a series of sharp fractions, M being obtained from measurements of light scattering or osmotic pressure and $[\eta]$ being measured as:

$$\lim_{c \to 0} \frac{\eta - \eta_0}{\eta_0 c}$$

or as:

$$\lim_{c \to 0} \frac{\ln (\eta/\eta_0)}{c}$$

Even with a given polymer sample, the values of K and a depend on the solvent used for the viscosity measurements[3] and, though to a lesser degree, on the temperature at which they were made[4].

For making measurements in a medium and not-too-wide (say, ten-fold) range of molecular weights, it does not seem to matter greatly which solvent is selected. The usual practice, however, is to use one of the good solvents for the polymer. In such a solvent, the value of $(\eta - \eta_0)/\eta_0 c$ or of $(\ln (\eta/\eta_0))/c$, is higher than in a poor solvent, and hence one can measure $[\eta]$ with greater precision.

For making measurements over a wide range of molecular weights, however, there are serious disadvantages in the use of a good solvent. One of these is that, in a good solvent, K and a are not true constants, but gradually change in value as the molecular weight of the polymer changes. This inconstancy of these "constants" has been observed with a variety of polymer-solvent systems, such as cellulose acetate in acetone[5], nitrocellulose in acetone[6], polyvinyl chloride in cyclohexanone[7], polyisobutylene in n-heptane[8], with polyesters in benzene[9]. It is, moreover, predicted by the current theories of intrinsic viscosity, such as those of Brinkman[10], Debye and Bueche[11], Kirkwood and Riseman[12], Peterlin[13], and Flory and Fox[14]. Indeed, for flexible linear molecules, a should vary in a good solvent from 1.00 at very low molecular weights to 0.50 at very high molecular weights.

* Reprinted from the *Journal of Polymer Science*, Vol. 13, Issue No. 68, pages 167–173, February 1954.

Another, and perhaps even more serious, disadvantage of a good solvent is that it accentuates shear effects. It has been known for years[15] that solutions of linear high polymers exhibit anomalous flow, the apparent viscosity decreasing with increasing rate of shear. With many polymers this effect is small enough to neglect with impunity, but, with those of high molecular weight, it most certainly is not[16]. Both the magnitude of the effect and the difficulty of correcting for it by extrapolating to zero rate of shear increase with increasing molecular weight, and both are much greater in a good than in a poor solvent[17] (see below).

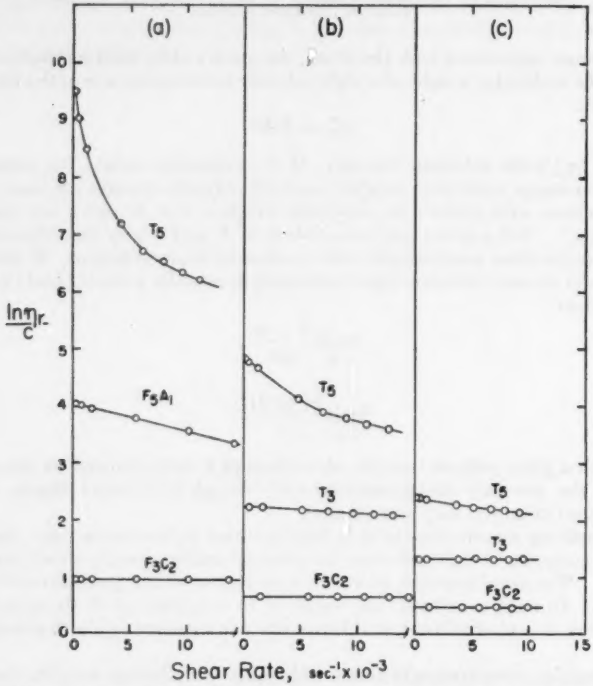


FIG. 1.—Effect on inherent viscosity *vs.* shear rate curves of varying the solvent: (a) toluene at 45° C, (b) cyclohexane at 65° C, (c) cyclohexane at 35° C. Molecular weights of polystyrene fractions used: T_5, 10×10^6; T_3, 2.4×10^6; F_5A_1, 2.2×10^6; F_3C_2, 0.3×10^6.

The use of a very poor solvent avoids these difficulties associated with the use of a good solvent, and has other virtues as well. Consider first the advantages.

(*1*) *In a very poor solvent, shear effects that are very troublesome in good solvents become negligible or easily manageable.* This influence of the magnitude of the shear effect is clearly demonstrated in Figure 1, in which values of $(\ln \eta_r)/c$—η_r being η/η_0—are plotted against the shear rate D for three polystyrene fractions: (*a*) in toluene at 45° C (a good solvent), (*b*) in cyclohexane at 65° C (a fair solvent), and (*c*) in cyclohexane at 35° C (at this temperature, a very poor

solvent). The solutions were of comparable concentrations, all in the range 0.07 ± 0.01 g./100 cc.; the polymers were close fractions of polystyrene, whose molecular weights were approximately 0.3×10^6, 2×10^6 and 9×10^6, calculated using the corrected equation of Fox and Flory[18]. (Experimental details are given elsewhere[22].) In the good solvent the shear effect is nil for the lowest fraction; appreciable for the middle one, unmanageable for the highest one; and extrapolation, though apparently safe for the middle fraction, is obviously unsafe for the highest one. When, however, the solvent power is sharply decreased, shear effects are reduced and extrapolation is made either safe or unnecessary. Clearly, the use of a very poor solvent makes possible the extension of the viscometric method to much higher molecular weights than could be determined in the usual (good) solvents.

(2) *In a very poor solvent, the values of K and a are constant over a wide range of molecular weights.*

According to the Flory-Fox interpretation[14] of the intrinsic viscosity of flexible chain molecules:

$$[\eta] = KM^{\frac{1}{2}}\alpha^3 \tag{2}$$

where K is, at a given temperature, a constant characteristic of the polymer, but independent of the solvent, and α is an "extensibility coefficient" which takes account of the effects of solvent, temperature, and molecular weight on the effective size of the "coiled" molecule. The coefficient α has the value of unity at the temperature θ, which is the critical miscibility temperature for the polymer homolog of infinite molecular weight and the temperature at which the osmotic slope constant B[22] is zero. A solvent at this temperature is, therefore, an "ideal" solvent[20], even though it is also a very poor solvent in the sense that we have been using the term "poor". It follows, then, that if the intrinsic viscosity is measured in a solvent at its θ-temperature—i.e., in an "ideal" solvent—the relation between $[\eta]$ and molecular weight becomes, simply:

$$[\eta]_\theta = KM^{\frac{1}{2}} \tag{3}$$

This relation has been shown to hold for a wide variety of linear polymers, including polyisobutylene[18], natural rubber[21], gutta-percha[21], polystyrene[22], and cellulose tributyrate and tricaprylate[23]. It certainly simplifies the calculation of molecular weights. Equation (3) may be written in the form:

$$M = \frac{1}{K^2}[\eta]^2_\theta \tag{4}$$

For polystyrene, for example, cyclohexane is a suitable solvent, its θ-temperature being 34.3° C. At this temperature K has the value[24] $8.1\ (\pm 0.2) \times 10^{-4}$ when it is expressed in the units[25] dl./g. Thus, when $[\eta]$ is measured in cyclohexane at 34.3° C:

$$M = 1.5_2 \times 10^6\,[\eta]^2$$

Recently Krigbaum and coworkers[26] have shown that Equation (3) is valid for the typical flexible polymers, polyisobutylene and polystyrene, over an extraordinarily wide range. With polystyrene one value of K used in Equation (3) or (4) gives molecular weights with good precision throughout the range 1×10^4 to 7×10^6.

It is worth emphasizing that, for any flexible polymer in any poor solvent at its θ-temperature (that is, in any "ideal" solvent), the a of Equation (1) not only is constant over a wide range of molecular weights but also has the same

value, 0.50, as in any other ideal solvent. And it has this same value for every linear flexible polymer. This means, in effect, that if the right choice of solvent is made one of the two "constants" of Equation (1) is already determined. This fact is of practical importance for molecular-weight determination, for it is easier to determine one empirical constant than two, and fewer measurements are required.

(3) *In a very poor solvent, extrapolation to zero concentration is easier, especially at very high molecular weights.*

There are two reasons why this should be so. Intrinsic viscosity is usually obtained by extrapolating the $(\eta_r - 1)/c$ *vs.* c line to $c = 0$. The smaller the slope of this line, the easier is the extrapolation. In a very poor solvent, the slope, $k'[\eta]^2$, is much less than in a good one, for although k' is increased in the

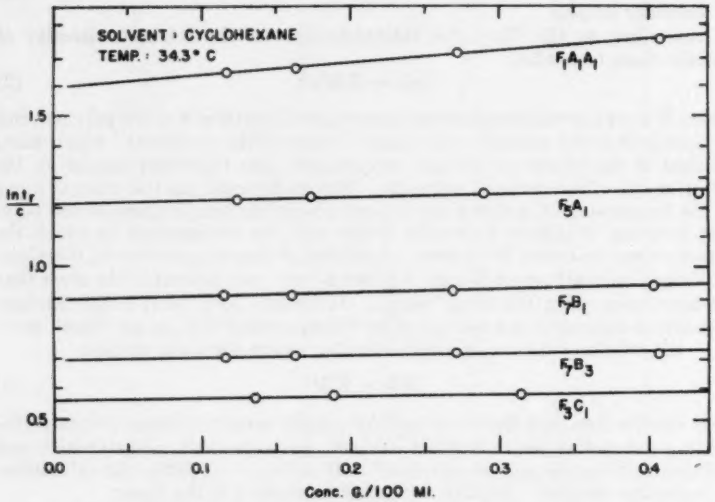


FIG. 2.—Typical inherent viscosity *vs.* concentration curves in an ideal solvent: Five polystyrene fractions in cyclohexane at 34.3° C. Molecular weights of fractions: $F_1A_1A_1$, 5.5×10^6; F_5A_1, 2.2×10^6; F_7B_1, 1.2×10^6; F_7B_3, 0.70×10^6; F_5C_1, 0.48×10^6.

very poor solvent, $[\eta]$ is decreased relatively more and $[\eta]^2$ is, therefore, decreased relatively much more. And if, as is often preferable, $[\eta]$ is obtained by extrapolating the $[(\ln \eta_r)/c]$ *vs.* c line to $c = 0$, the extrapolation is very easy indeed in the poor solvent, for then the slope of this line is very small, even at very high molecular weights. See, for example, Figure 2.

The second reason is that, with very high polymers, the lines to be extrapolated are more apt to be straight lines in the very poor solvents. The linear equations:

$$(\eta_r - 1)/c = [\eta] + k'[\eta]^2 c \tag{5}$$

and:

$$(\ln \eta_r)/c = [\eta] - \beta[\eta]^2 c \tag{6}$$

adequately represent experimental data obtained with most polymers in dilute solutions. But if either the concentration of the solution or the molecular

weight of the polymer is sufficiently increased, the line becomes curved, and Equations (5) and (6) fail (unless higher terms in c are added). Either increasing the volume of the polymer molecules (by increasing their weight), or crowding them closer together (by increasing the concentration of the solution), increases the probability of the mutual interference which, apparently, is the cause of the curvature in these lines. Changing from a good to a poor solvent has the effect of coiling the molecules up into tighter balls, and hence should have an effect similar to that of decreasing the molecular weight or lowering the concentration. As Boyer and Simha[27] have recently pointed out, this advantage might "more than compensate for the apparent loss in accuracy in using a poorer solvent".

There are also disadvantages in the use of a very poor solvent, but fortunately most of these can readily be overcome.

1. In a very poor solvent, $[\eta]$ is smaller and, therefore, the precision of measurement is lower. This is an important consideration at the low end of the molecular-weight range only. There, greater precision can be achieved by making measurements at higher concentrations (so that values of η_r remain in the range 1.15–1.6); and, if necessary, a good solvent can be used.

2. The specification that the solvent should be "very poor", combined with the practical requirement that measurements should be made at a convenient temperature, severely restricts the choice of solvent. This is particularly true if, as is desirable, the solvent is to be used at its θ-temperature. However, if a simple ideal solvent is not found, measurements can be made in a suitable mixed solvent—i.e., a solvent-nonsolvent mixture such that the θ-temperature is a convenient temperature for viscosity measurements[28].

3. In a very poor solvent, there is greater danger of molecular association[29]. It is probable that, even in systems where such association could be significant, any appreciable effects on viscosity-measured molecular weights could be avoided by making measurements immediately after the solutions are prepared. However, it is not necessary to assume that association is thus forestalled, for association where it does occur may readily be detected[29].

From all this we conclude that the advantages of using an "ideal" solvent outweigh the disadvantages and, for very high molecular-weight polymers, the choice of the "ideal" solvent seems inevitable. It is surely significant that, as Boyer and Simha have so clearly stated[27], an "ideal" solvent is the best choice in many other molecular-weight determinations, including those involving the measurement of light scattering, osmotic pressure, and sedimentation equilibrium.

SYNOPSIS

For the viscometric determination of the molecular weight of a flexible linear high polymer, a very "poor" solvent, in which the osmotic slope constant B is zero, i.e., a so-called "ideal" solvent, has several advantages over the usually preferred good ones. For example, shear effects that are very troublesome with very high polymers become negligible or easily manageable in good solvents. Moreover, in an "ideal" solvent, the "contents" K and a in the equation relating $[\eta]$ and M really are constant over a wide range of molecular weights and, since a always has the value 0.50, are more easily determined. Because the advantages seem to outweigh considerably the disadvantages, the use of an "ideal" solvent should be given careful consideration, particularly when the molecular weights are very high or cover a wide range.

REFERENCES

[1] Mark, "Die Feste Korper", Hirzal, Leipzig, **1938**, p. 103; Houwink, *J. prakt. Chem.* **157**, 15 (1940).
[2] Flory, *J. Am. Chem. Soc.* **65**, 372 (1943).
[3] Bawn, Grimley, and Wajid, *Trans. Faraday Soc.* **46**, 1112 (1950).
[4] Alfrey, Bartevics, and Mark, *J. Am. Chem. Soc.* **65**, 2319 (1943).
[5] Badgley, *Polymer Bull.* **1**, 17 (1945).
[6] Münster, *J. Polymer Sci.* **8**, 633 (1952).
[7] Hengstenberg, *Angew. Chem.* **62**, 26 (1950).
[8] Kunst, *Dissertation*, Groningen, **1950**.
[9] Batzer, *Makromol. Chem.* **5**, 5 (1950).
[10] Brinkman, *Physica* **13**, 447 (1947).
[11] Debye and Bueche, *J. Chem. Physics* **16**, 573 (1948).
[12] Kirkwood and Riseman, *J. Chem. Physics* **16**, 565 (1948).
[13] Peterlin, *J. Polymer Sci.* **5**, 473 (1950).
[14] Flory and Fox, *J. Am. Chem. Soc.* **73**, 1904 (1951).
[15] Staudinger, "Die Hochmolekularen Organischen Verbindungen", Springer, Berlin, **1932**, p. 189.
[16] Conrad, Tripp, and Mares, *J. Phys. & Colloid Chem.* **55**, 1474 (1951); Fuoss and Maclay, *J. Polymer Sci.* **6**, 305 (1951); Fox, Fox, and Flory, *J. Am. Chem. Soc.* **73**, 1901 (1951); Akkerman, Pals, and Hermans, *Rec. trav. chim.* **71**, 56 (1952); Sharman, Sones, and Cragg, *J. Applied Physics* **24**, 703 (1953).
[17] Sharman, Sones, and Cragg, *J. Applied Physics* **24**, 703 (1953).
[18] Fox and Flory, *J. Am. Chem. Soc.* **73**, 1915 (1951).
[19] Huggins *et al.*, "Report on Nomenclature in the Field of Macromolecules", *J. Polymer Sci.* **8**, 257 (1952).
[20] Hildebrand and Scott, "Solubility of Nonelectrolytes", Reinhold Publishing Corp., New York, 3rd Ed., **1950**, p. 357.
[21] Wagner and Flory, *J. Am. Chem. Soc.* **74**, 195 (1952).
[22] Fox and Flory, *J. Am. Chem. Soc.* **73**, 1915 (1951); Cragg, Dumitri, and Simkins, *J. Am. Chem. Soc.* **74**, 1977 (1952).
[23] Mandelkern and Flory, *J. Am. Chem. Soc.* **74**, 2517 (1952).
[24] The values for θ and K are those determined in this laboratory (see Dumitri, *M.Sci. Thesis*, McMaster University, **1952**). They agree, well within the experimental error, with those obtained by Schultz (see A. R. Schultz, private communication, Cornell University), *viz.*, 34° C and 8.2×10^{-4}.
[25] When $[\eta]$ is expressed in the units, cc. per g., and is, therefore, the "limiting viscosity number" (see Huggins *et al.*, "Report on the Nomenclature in the Field of Macromolecules", *J. Polymer Sci.* **8**, 257 (1952), the corresponding value of K would be 100 times greater, *viz.*, 8.1×10^{-2}.
[26] Krigbaum, Mandelkern, and Flory, *J. Polymer Sci.* **9**, 381 (1952); Krigbaum and Flory, *J. Polymer Sci.* **11**, 37 (1953).
[27] Boyer and Simha, in Boundy and Boyer, "Styrene", Reinhold Publishing Corp., New York, **1952**.
[28] See, for example Mandelkern and Flory, *J. Am. Chem. Soc.* **74**, 2517 (1952).
[29] Doty, Wagner, and Singer, *J. Phys. & Colloid Chem.* **51**, 32 (1947).

CHROMATOGRAPHIC ANALYSIS OF VULCANIZED RUBBERS

SPECIFIC METHODS FOR THE DETECTION OF SOME DITHIOCARBAMATE ACCELERATORS *

C. A. PARKER AND JOYCE M. BERRIMAN

ADMIRALTY MATERIALS LABORATORY, HOLTON HEATH, POOLE, DORSET, ENGLAND

INTRODUCTION

The formation of highly colored metallic complexes by certain accelerators has frequently been applied to the detection of these compounds in the solvent extracts of vulcanized rubbers[1]. For the detection of dithiocarbamates, copper oleate in chloroform[2] or benzene[3], copper sulfate in aqueous acetone[4], aqueous copper sulfate with carbon tetrachloride or benzene[5], aqueous copper acetate with chloroform[6], cobalt oleate in benzene[7], aqueous nickel sulfate[8], nickel, lead, uranium and ferric oleates in benzene[3], and cobalt chloride, uranyl nitrate, nickel chloride, and copper butyl phthalate in alcohol-benzene[3] have all been investigated. Spot tests based on such reagents are satisfactory in simple cases where only one color-producing compound is present. In general, however, the colors obtained with acetone extracts do not make possible specific identification and, in many cases, are obscured by other colored compounds present. Bellamy, Lawrie, and Press[3] overcame this difficulty by subsequent chromatographic separation of the colored metallic complexes on alumina, but applied the method only to a few selected accelerators.

The great selectivity of silica gel in separating a wide variety of accelerators and antioxidants[9], suggested that this adsorbent might prove satisfactory for the separation of the closely related alkyl dithiocarbamates from one another and from other rubber ingredients. The zinc dithiocarbamates can be chromatographed directly on silica gel[10], their zones being detected by streaking with copper sulfate solution. This method suffers from several disadvantages. The zones produced are generally diffuse, and the streak reactions may be confused with those of other compounds giving yellow colors with copper sulfate. Preliminary experiments showed that chromatography of the brown copper complexes does not suffer from either of these disadvantages. Tight zones are obtained, which are readily separated from those of other colored compounds. This method has, therefore, been investigated in detail.

COMPOUNDS STUDIED

The six simplest alkyl dithiocarbamates were chosen for study. Four of these are commonly used as accelerators, either as their zinc or amine salts. Certain of them also occur as decomposition products of thiurams. The propyl compounds are not normally used commercially, but were included to complete the series.

* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 30, No. 3, pages 69–75, June 1954.

All the amine salts were prepared by the reaction of redistilled carbon disulfide with the purified amine in ethyl alcoholic solution, followed by recrystallization of the compound from alcohol. ZDC and ZNBC were prepared by several recrystallizations of the commercial materials. The remaining zinc compounds were prepared from the amine salts by treatment with zinc acetate and recrystallization from ethyl or butyl alcohol. The melting points of the products are compared in Table I with those reported in the literature.

PREPARATION OF COPPER DERIVATIVES

The copper derivatives were prepared by treating an aqueous solution of the amine salt with 1 per cent aqueous copper sulfate solution and extracting with carbon tetrachloride, or, in the case of the zinc salts, by shaking a 0.1 per cent solution of the dithiocarbamate in carbon tetrachloride with the copper sulfate

TABLE I

Abbreviation	Compound	Melting point	
		Found (° C)	Literature (° C)
MMC	Dimethylamine dimethyldithiocarbamate	133°	132°[11]
ZMC	Zinc dimethyldithiocarbamate	253°	243–5°[11]
DDCN	Diethylamine diethyldithiocarbamate	82°	81°
ZDC	Zinc diethyldithiocarbamate	181°	180°[13]
DPC	Di-*n*-propylamine di-*n*-propyldithiocarbamate	118°	114°[13]
ZPC	Zinc di-*n*-propyl dithiocarbamate	110°	—
DIC	Di-iso-propylamine diisopropyldithiocarbamate	decomposes at 114°	110°[11]
ZIC	Zinc diisopropyl dithiocarbamate	decomposes at 207°	—
ZNBC	Zinc di-*n*-butyl dithiocarbamate	110°	110°[11]
PPD	Piperidine pentamethylenedithiocarbamate	sublimes (m.p. 168–9 in sealed tube)	167–72°[11]
ZPD	Zinc pentamethylenedithiocarbamate	229°	222–5°[11]

solution. Owing to the small solubility of the copper complex of the dimethyl compound in carbon tetrachloride, benzene was used for this compound. The solution of the copper complex was washed twice with water, dried over anhydrous sodium sulfate, and filtered.

This and all other procedures were carried out in subdued light, owing to the photosensitivity of the copper compounds[14].

CHROMATOGRAPHIC BEHAVIOR OF COPPER DERIVATIVES

One-mg. quantities of the copper complexes were placed on 1 × 15 cm. columns of silica gel-celite[14] in 1 cc. of carbon tetrachloride or benzene[15] and developed with 25–50 cc. of the appropriate solvent mixture. The following binary developers were investigated: ethyl ether—light petroleum, ethyl acetate—light petroleum, benzene—light petroleum, methylene chloride—carbon tetrachloride, benzene—carbon tetrachloride, ethyl ether—carbon tetrachloride, and ethyl acetate—carbon tetrachloride. Of these, the last two gave the tightest zones, and of these two, ethyl ether in carbon tetrachloride gave slightly better separations. Figures 1–3 show the positions of the zones obtained with the chosen concentrations of ethyl ether. It was found that as little as 0.05 mg.

of the copper dithiocarbamates produce a visible zone on the column. This corresponds to the detection of 0.01 per cent of the accelerators in the original rubber when the normal 0.4 gram sample is taken for extraction.

An interesting chromatogram was obtained from the piperidine pentamethylene dithiocarbamate. The copper complex produced two zones on the column, which were separated by development with 1 per cent ethyl ether in carbon tetrachloride (see Figure 2). When the zones were eluted separately and rechromatographed, they developed as single zones to their original positions, showing that they were not produced by decomposition on the column. The absorption spectra of these two compounds showed maximum light absorption at a wave length characteristic of copper alkyldithiocarbamates, and indicated that the two constituents were present in approximately equal amounts. (Similar zones were obtained from commerical PPD accelerator.) By careful fractional distillation of piperidine, a pure fraction was obtained, with a boiling range of 105.5–105.9° C. From this piperidine a fresh sample of

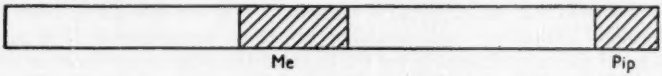


FIG. 1.—Two per cent ethyl ether (placed in benzene solution).

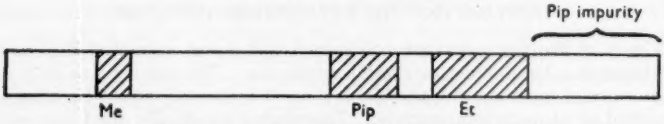


FIG. 2.—One per cent ethyl ether (placed in CCl_4 solution).

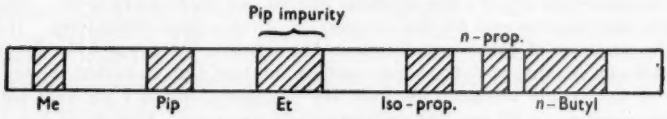


FIG. 3.—One-half per cent ethyl ether (placed in CCl_4 solution).

piperidine pentamethylenedithiocarbamate was prepared, which, when chromatographed as the copper derivative, gave one principal zone, with only a slight trace of impurity appearing as a second faint zone. The purer copper salt appeared less soluble in carbon tetrachloride than the impure material. From the distillation of the piperidine a second fraction was also obtained, with a boiling range of 108.0–116.8° C. The amine dithiocarbamate prepared from this material, when converted to the copper complex, produced a strong zone on the column, corresponding in position to that of the impurity in the original material. Further investigation of the higher boiling fraction showed that it contained large quantities of tetrahydropyridine.

The chromatographic procedures were next applied to mixtures of adjacent pairs of compounds in the adsorption series (Figures 1–3). It was found that the presence of more than one compound altered slightly the position of the zones, but separations were still possible with the quoted developers except in the case of the *n*-propyl and *n*-butyl compounds, where 40 cc. of 0.25 per cent ethyl ether/carbon tetrachloride had to be used to obtain a separation. It was also found that the presence of other normal compounding ingredients some-

times increased slightly the development of the copper dithiocarbamate zones. In such cases, the identity of a zone could easily be confirmed by adding 1 mg. of the suspected copper dithiocarbamate to the rubber extract before chromatography, and observing whether the two zones coincided.

When chromatographing mixtures of dithiocarbamates, two sets of conditions were investigated, namely, mixing the compounds before reaction with copper sulfate and mixing the copper complexes after their separate formation. In the case of the methyl and piperidyl compounds, it was found that an additional zone was produced by combining the dithiocarbamates before treatment with copper sulfate. This was a weak zone appearing above the methyl zone on the column and was assumed to be due to a mixed piperidyl-dimethyl copper complex. It did not interfere with the identifications. It was noticed that the presence of a second dithiocarbamate in the solution (to be treated with copper sulfate and extracted with carbon tetrachloride) caused a much stronger methyl or piperidyl zone to be produced. Likewise, by mixing the methyl and piperidyl amine salts themselves, much stronger zones of their copper complexes were produced than when prepared separately. As the strength of these zones is normally limited by their solubility in carbon tetrachloride, it is possible that molecular complexes between the dithiocarbamates are produced in carbon tetrachloride solution which have the effect of increasing the solubility.

APPLICATION TO VULCANIZED RUBBERS

Ten g. of the finely divided vulcanized rubber was extracted with acetone for 8 hours in a hot Soxhlet-extraction apparatus. The extract was evaporated under reduced pressure, and the last few cc. of acetone removed by means of a current of air at room temperature. The residue was finally dried over sulfuric acid. It was then extracted with several portions of warm carbon tetrachloride (or benzene—see above), the solutions filtered and made up to 25 cc. Ten cc. of this solution was used for the preparation of the copper derivatives. Owing to the presence of other ingredients in the extract, there was a tendency to emulsify on shaking with the copper sulfate solution and, to hasten the separation of the carbon tetrachloride from the aqueous phase, a 1 per cent copper sulfate solution in 15 per cent sodium sulfate was used. One cc. of the dried carbon tetrachloride (or benzene) solution was taken for chromatography.

The methods were applied to six vulcanizates in which the following accelerators had been used: ZMC, ZDC, SDC (sodium diethyldithiocarbamate), ZNBC, PPD, and Vulcafor DHC. (The latter was a commercial accelerator which was found to contain both ZDC and mercaptobenzothiazole). The other components of the mixes were as follows:

Rubber	69.7 per cent
Paraffin wax	0.7 per cent
Pine tar	3.5 per cent
Sulfur	1.7 per cent
Stearic acid	2.1 per cent
Zinc oxide	3.5 per cent
Carbon black	17.4 per cent
Phenyl-β-naphthylamine	0.7 per cent
Dithiocarbamate	0.7 per cent

Time of cure was 5 minutes at 141° C for ZMC, ZDC and ZNBC, 10 minutes at 141° C for DHC and SDC, and 5 minutes at 100° C for PPD.

It was found that the other ingredients of the acetone extract increased slightly the development of the zones, but did not otherwise interfere with

their identification. Pine tar is only partly soluble in the carbon tetrachloride used for placing the mixtures on the columns. The soluble portion produces a brown zone at the top of the columns and no other colored zones which could interfere with the detection of the dithiocarbamates. The zinc and amine dithiocarbamates are readily extracted from the carbon tetrachloride—insoluble material.

The dithiocarbamate was detected in the hot acetone extracts of all rubbers except that accelerated with PPD. The ZMC and ZDC rubbers produced strong zones, due to the accelerator. The residual dithiocarbamate was much less in the case of ZNBC or DHC. A second compound giving a brown copper complex was present in small amount in the ZNBC rubber, presumably a transformation product. A faint copper diethyldithiocarbamate zone was produced by the rubber accelerated with SDC and was assumed to be due to the presence of ZDC formed during vulcanization.

No piperidyl compound could be detected in the PPD rubber when it was extracted in a Soxhlet apparatus with boiling acetone. Further experiments showed that PPD is completely decomposed by prolonged boiling with a rubber extract in acetone. A second attempt to identify the pentamethylenedithiocarbamate was therefore made, using a cold acetone extract, and this was entirely successful. This decomposition of the PPD, which is particularly severe in the presence of other compounding ingredients, may explain the experience of Mann[16], who was unable to detect PPD in a rubber accelerated with it, although in rubber accelerated with ZPD, he was able to detect some unchanged accelerator. Experiments with the other amine salts have shown that, although they undergo minor decomposition during hot acetone extraction, the effect is small compared with that observed with PPD, and does not prevent the subsequent identification of dithiocarbamate. However, our experience with the amine dithiocarbamates emphasizes the need for extreme care in the choice of extraction conditions when dealing with certain accelerators. As a further example of this, the decomposition of TMT during extraction may be quoted. With this accelerator, extraction even with cold acetone caused decomposition, and it was found necessary to employ cold methylene chloride before TMT could be recovered[10].

The methods for the detection of the dithiocarbamates were also applied to rubbers accelerated with the following compounds: tetramethylthiuram disulfide (TMT), tetraethylthiuram disulfide (TET), and tetramethylthiuram monosulfide (MS). ZMC was detected in quantity in the TMT and MS rubbers, and ZDC in the TET rubber. This is in agreement with the results of previous workers[17], who have obtained evidence of the extensive conversion of thiuram mono- and disulfides to dithiocarbamates during vulcanization.

ADVANTAGES OF THE PROPOSED METHODS

The methods are rapid and specific and will distinguish between the six simplest dithiocarbamates. They can be applied in the presence of other normal compounding ingredients or accelerator transformation products. In particular, other colored compounds in the extract do not interfere, as is the case with the more usual spot tests recommended by previous workers. The methods are sensitive (0.01 per cent of dithiocarbamate can be detected using only 0.4 gram of rubber) and with minor modification can be adapted to the separation of the compounds prior to their quantitative spectrophotometric determination.

SUMMARY

Methods are described for the mutual separation and identification of six alkyl-substituted dithiocarbamates by chromatography of their brown copper complexes on silica gel. These methods have been successfully applied to the detection of dithiocarbamates in vulcanized rubbers, and they form an extension to the scheme for the chromatographic identification of accelerators and antioxidants reported in a previous communication[9].

ACKNOWLEDGMENT

This paper is published by permission of the Admiralty.

REFERENCES

[1] Shimada, *J. Soc. Chem. Ind. Japan* **37**, 82, 262 (1933); *India-Rubber J.* **96**, 380, 415, 446 (1938); Slepuschkina, *India-Rubber J.* **95**, 290 (1938); Schaefer, *Gummi-Ztg.* **55**, 400 (1941); *India-Rubber J.* **105**, 303 (1943); *Kautschuk u. Gummi* **1**, 149 (1948); RUBBER CHEM. & TECHNOL. **23**, 292 (1950); Morrison and Shepherd, *Trans. Inst. Rubber Ind.* **22**, 189 (1946); Kulberg and Blokh, *Zavodskaya Lab.* **14**, 278 (1948); Bellamy, Lawrie, and Press, *Trans. Inst. Rubber Ind.* **22**, 308 (1947); Kulberg, Blokh, and Golybkova, *Zavodskaya Lab.* **15**, 1034 (1949); Burmistrov, *Zavodskaya Lab.* **15**, 1039; RUBBER CHEM. & TECHNOL. **25**, 157 (1952).

[2] Morrison and Shepherd, *Trans. Inst. Rubber Ind.* **22**, 189 (1946).

[3] Bellamy, Lawrie, and Press, *Trans. Inst. Rubber Ind.* **22**, 308 (1947).

[4] Schaefer, *India-Rubber J.* **105**, 303 (1943); *Kautschuk* **1**, 149 (1948); RUBBER CHEM. & TECHNOL. **23**, 292 (1950); Budig, *Kautschuk u. Gummi* **4**, 47 (1951).

[5] Schaefer, *Gummi-Ztg.* **55**, 400 (1941).

[6] Kulberg, Blokh, and Golybkova, *Zavodskaya Lab.* **15**, 1034 (1949); RUBBER CHEM. & TECHNOL. **25**, 152 (1952).

[7] Shimada, *J. Soc. Chem. Japan* **36**, 82, 262 (1933); *India-Rubber J.* **96**, 380, 415, 446 (1938); Bellamy, Lawrie, and Press, *Trans. Inst. Rubber Ind.* **22**, 308 (1947).

[8] Shimada, *J. Soc. Chem. Ind. Japan* **36**, 82, 262 (1933).

[9] Parker, *Nature* **170**, 539 (1952); RUBBER CHEM. & TECHNOL. **26**, 447 (1953); Parker and Berriman, *Trans. Inst. Rubber Ind.* **28**, 279 (1952); RUBBER CHEM. & TECHNOL. **26**, 449 (1953).

[10] Parker and Berriman, *Trans. Inst. Rubber Ind.* **28**, 279 (1952); RUBBER CHEM. & TECHNOL. **26**, 449 (1953).

[11] Robinson, *Trans. Inst. Rubber Ind.* **14**, 49 (1939).

[12] Heilbron, "Dictionary of Organic Compounds", Eyre and Spottiswoode, **1934**, Vol. 1, p. 515.

[13] Whitby and Matheson, *Trans. Roy. Soc. Can.* [3], **18**, III, 111 (1924).

[14] Ovenston and Parker, *Anal. Chim. Acta* **4**, 135 (1950).

[15] Two cc. of a saturated solution of the copper complex of the dimethyl compound in carbon tetrachloride contains sufficient to produce a weak brown zone. One cc. of a saturated solution in benzene produces a strong zone; benzene was, therefore, used when testing for the dimethyldithiocarbamate. It cannot, however, be used for placing the other compounds because of their weak adsorption from this solvent.

[16] Mann, *Trans. Inst. Rubber Ind.* **27**, 232 (1951).

[17] Jones and Depew, *Ind. Eng. Chem.* **23**, 1467 (1931); Shepard, *Ind. Eng. Chem.* **26**, 1200 (1934); Shimada, *India-Rubber J.* **96**, 380, 415, 446 (1938); Dufraisse and Jarrijon, *Compt. rend.* **215**, 181 (1942); Morrison and Shepherd, *Trans. Inst. Rubber Ind.* **22**, 189 (1946); Bellamy, Lawrie, and Press, *Trans. Inst. Rubber Ind.* **22**, 308 (1947); Mann, *Trans. Inst. Rubber Ind.* **27**, 232 (1951); Craig, Davidson, and Juve, RUBBER CHEM. & TECHNOL. **24**, 275 (1951).

AN INSTRUMENT FOR DETERMINING THE RELAXATION AND RECOVERY OF ELASTOMERS *

B. G. LABBE AND W. E. PHILLIPS

GOVERNMENT LABORATORIES, UNIVERSITY OF AKRON, AKRON, OHIO

The search for an improved method to determine the properties of elastomers at low temperatures has uncovered a wide variety of methods. The majority of these procedures employs equipment formerly used at room temperatures, or equipment modified to permit operation at temperatures as low as −80° C. The Gehman low-temperature test,[1] determination of Young's modulus,[2] resilience by the Yerzley oscillograph,[3] and the T-50 relaxation tests[4] are a few of the more prominent procedures available at present. The ASTM compression set method B[5] has been quite popular for determining permanent set of elastomers at elevated temperatures and has also been used at temperatures as low as −70° F. While this methods shows what will happen when the sample is allowed to recover freely after compression, it does not indicate the force required to compress the sample or the rate of relaxation of forces within the sample during compression resulting from changes in time or temperature.

The development of freeze resistant polymers and the testing of the compounded stocks showed the need for an instrument that would determine the force required to produce definite degrees of compression at temperatures as low as −70° F, and indicate both the rate of relaxation of the load and the change of load when the platens are separated after compression.

MacDonald and Ushakoff[5] described an instrument in which a test-specimen can be subjected to a definite percentage compression or to any given load and which, by means of a strain gauge and recording device, shows the relaxation of the forces within the test-specimen as time progresses. The Government Laboratories designed a similar instrument which permits gradual instead of instantaneous loading of samples, enables the operator to increase and decrease the compression during the test, and provides means of determining the recovery characteristics of specimens under test.

DESCRIPTION OF INSTRUMENT

A schematic drawing of the instrument is presented in Figure 1. The overall height is about 14 inches, and the diameter, 5½ inches. The jig used to compress the test specimen consists of a Baldwin SR-4 Type C load cell[6] of 2000-pound capacity, a gear and screw arrangement to permit application of the load to the test specimen, and a crank and counter assembly to indicate the thickness of the loaded test specimen. The height of the lower platen is changed 0.05-inch by one complete revolution of the large gear. The ratio of the large gear to the crankshaft gear is 5:1; thus one revolution of the latter raises or lowers the platen 0.01-inch. The dial on the crankshaft at the counter is graduated in tenths and provides the means of reading a height change of 0.001-inch. A Foxboro Dynalog[7] measures the voltage output of the strain-gage bridge to record the force exerted by the test pellet.

* Reprinted from the *India Rubber World*, Vol. 129, No. 10, pages 489–491, January 1954. The work was carried out under the sponsorship of the Office of Synthetic Rubber, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program. The paper was presented at the 53rd Meeting of the Division of Rubber Chemistry of the American Chemical Society, Detroit, Michigan, November 8–10, 1948.

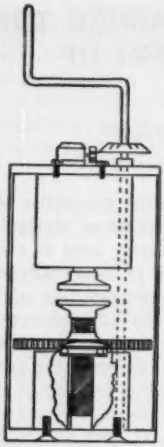


FIG. 1.—Schematic drawing of stress relaxation jig.

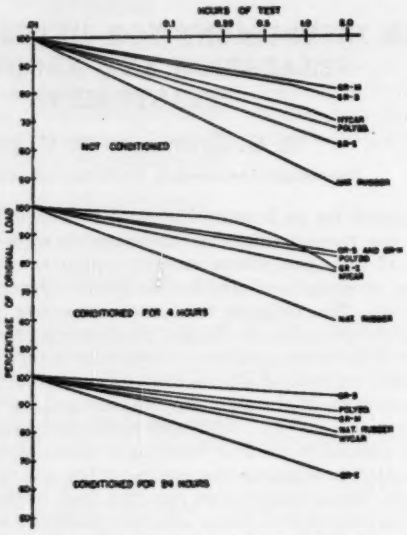


FIG. 2.—Stress-relaxation tests at 212° F.

PROCEDURE

The following compounding recipes and the elastomers indicated were used in this investigation:

GR-S	
GR-S	100
EPC black	50
Zinc oxide	5
Stearic acid	1.5
Paraflux	5
N-cyclohexyl-2-benzothiazole sulfenamide	1.2
Sulfur	1.75

Natural rubber	
Smoked sheet	100
EPC black	50
Zinc oxide	5
Stearic acid	3
Paraflux	3
Phenyl-beta-naphthylamine	1
Captax (Mercaptobenzothiazole)	1
Sulfur	3

Nitrile rubber	
Hycar (OR-25)	100
SRF black	100
Zinc oxide	5
Dibutyl phthalate	25
Benzothiazyl disulfide	1
Sulfur	1

Polybutadiene	
Polybutadiene (polymerized at 122° F)	100
EPC black	50
Zinc oxide	5
Stearic acid	1.5
Paraflux	5
Santocure	1.2
Sulfur	1.75

Butyl	
GR-I	100
EPC black	20
SRF black	30
Zinc oxide	5
Petrolatum	3
Captax	0.5
Methyl Tuads (tetramethylthiuram disulfide)	1
Sulfur	2

Neoprene	
Neoprene	100
Phenyl-alpha-naphthylamine	2
Stearic acid	0.5
Light calcined magnesia	4
MT black	57.6
Petroleum processing oil	20
Sulfur	1
Zinc oxide	5

From stress-strain data for these compounds, the optimum cure for each was selected, and 0.5-inch slabs were vulcanized for 10 minutes more than the optimum time. Because the standard ASTM pellet, 1.129 inches in diameter, taxed the capacity of the load cell when tests were conducted on specimens aged at low temperatures, a cylindrical test-specimen 0.7-inch in diameter and 0.5-inch high was used. The testing procedure consisted in placing the test-pellet in the center of the lower platen and then raising it against the rigid upper platen by means of the crank and gear assembly. The sample was compressed 40 per cent, and the force on the load cell was automatically recorded on the Foxboro Dynalog. The test-specimen was permitted to relax for 100 minutes at 40 per cent compression; then the aperture was increased by 0.005 or 0.10 inch, depending on the testing temperature. As the sample recovered from its deformation, the stress applied to the strain-gauge bridge was recorded by the Dynalog. Since the initial portion of the relaxation curve is extremely steep, the method initiated by MacDonald and Ushakoff was adopted. Instead of considering the peak load as the zero relaxation point, they adopted the extrapolated stress at 0.6 minute. This extrapolation was made from a graph drawn by plotting the actual stress applied as ordinate against time on a logarithmic scale as abscissa. With this derived value as the initial stress, the relaxation at any given time may be calculated as follows:

$$\% \text{ Relaxation} = 100\% - \left\{ \frac{\text{stress at given time}}{\text{extrapolated initial stress}} \times 100 \right\}.$$

Although this testing procedure was used for the majority of tests with this apparatus, preliminary experiments were conducted with variations in the described method. Tests were conducted at 212°, 158°, 75°, −20°, −40°, and −70° F. In addition, specimens were conditioned for both 4 and 24 hours at 212°, −20°, and −40° F prior to loading.

DISCUSSION

MacDonald and Ushakoff[6] reported that the change in relaxation of several elastomers tested at room temperature is linear with the logarithm of time. Data obtained with the instrument developed at the Government Laboratories verified this observation when tests were conducted over a period of 100 minutes at room temperature. At 212° and −20° F and at lower temperatures, several tests indicated that some of the elastomers exhibit a nonuniform rate of relaxation with log time. This nonuniformity is probably caused by additional vulcanization or aging of the sample at the higher temperatures and by a form of crystallization at the lower temperatures.

Table 1 presents the pertinent data obtained with the six compounds over the range of temperatures investigated. The percentage of original load and relaxation after 100 minutes and the subsequent recovery values are shown.

To calculate the recovery values, the load measured 15 minutes after increasing the aperture between the platens was divided by the extrapolated initial stress. The distance between platens was increased by 0.005 inch for tests conducted at −20° F or lower and by 0.01 inch when the temperatures were 75° F or higher.

Practically all the graphs are similar to Figure 2. The actual relaxation is the difference between the percentage of original load and 100 per cent. For example, the Neoprene line of the "not conditioned" sample at 100 minutes shows 81.2 per cent of the original load or 18.8 per cent relaxation. In con-

Table 1

Stress Relaxation Data

Raw material in compound	Hours conditioned	212° F			158° F			75° F			Minus 20° F			Minus 40° F			Minus 70° F		
		% of original load*	% relaxation*	% recovery†	% of original load*	% relaxation*	% recovery†	% of original load*	% relaxation*	% recovery†	% of original load*	% relaxation*	% recovery†	% of original load*	% relaxation*	% recovery†	% of original load*	% relaxation*	% recovery†
GR-S	None	78.0	22.0	63.4	88.5	11.5	76.9	87.6	12.4	74.2	100.	0	83.7	97.1	2.9	76.9	100.0	0	36.0
Polybutadiene		67.7	32.3	54.1	82.9	17.1	71.1	84.8	15.2	72.6	94.5	5.5	78.6	94.1	5.9	78.6	90.8	9.2	71.1
Natural rubber		47.6	52.4	34.3	83.9	16.1	69.9	86.8	13.2	71.3	91.5	8.5	75.7	98.7	1.3	77.3	98.3	1.7	67.9
Butyl		61.4	38.6	50.0	87.1	12.9	75.8	94.4	5.6	83.6	96.7	3.3	83.6	100.0	0	85.9	100.0	0	73.9
Neoprene		81.2	18.8	70.5	90.0	10.0	79.0	86.3	13.7	75.1	100.0	0	86.9	97.5	2.5	79.4	78.3	21.7	13.3
Nitrile rubber		69.6	30.4	56.0	85.6	14.4	70.6	84.1	15.9	66.3	87.8	12.2	76.0	97.4	2.6	48.7	85.6	14.4	3.4
GR-S	4	83.1	16.9	71.4							78.6	21.4	69.2	42.0	58.0	34.2			
Polybutadiene		82.3	17.7	68.6							79.3	20.7	67.5	78.4	21.6	65.5			
Natural rubber		59.7	40.3	46.0							81.2	18.8	65.0	75.8	24.2	60.4			
Butyl		76.8	23.2	63.5							80.6	19.4	71.1	69.4	30.6	59.4			
Neoprene		83.2	16.8	72.6							83.7	16.3	73.1	54.9	45.1	41.6			
Nitrile rubber		76.1	23.9	59.8							44.1	55.9	33.8	—	—	—			
GR-S	24	92.7	7.3	81.3							75.6	24.4	65.7	56.3	43.7	47.8			
Polybutadiene		87.4	12.6	75.6							83.0	17.0	70.6	75.9	24.1	64.4			
Natural rubber		79.8	20.2	66.9							79.7	20.3	62.7	77.5	22.5	60.8			
Butyl		64.4	35.6	54.6							81.9	18.1	70.9	75.3	24.7	65.0			
Neoprene		84.5	15.5	74.7							83.2	16.8	72.7	64.3	35.7	55.7			
Nitrile rubber		78.0	22.0	64.5							43.0	57.0	33.8	—	—	—			

* After 100 minutes.

† Fifteen minutes after aperture between platens was increased by 0.010 inch.

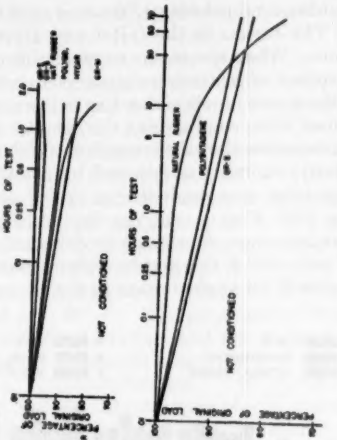


FIG. 5.—Stress-relaxation tests at −70° F.

FIG. 6.—Stress-relaxation tests at −20° F; 70-hour test.

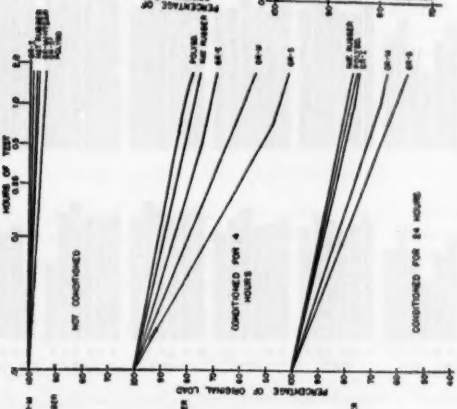


FIG. 4.—Stress-relaxation tests at −40° F.

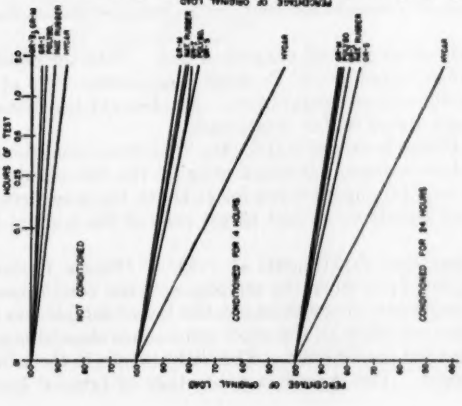


FIG. 3.—Stress-relaxation tests at −20° F.

trast, natural rubber retained only 47.6 per cent of the original load and relaxed 52.4 per cent. The breaks in the GR-S and Hycar lines indicate changes of rate of relaxation. When specimens were conditioned for four hours previous to loading, the spread of relaxation values narrowed, and the first drastic variation from a uniform rate of relaxation was indicated by the Butyl rubber curve. The curve obtained after conditioning the samples for 24 hours at 212° F previous to loading indicates that the transition which caused a nonuniform rate of relaxation for Butyl rubber was followed by a return to a uniform relaxation rate. No further tests were conducted at 212° F after it was learned that temperatures above 150° F may damage the bond of the strain-gauge bridge. These data must, therefore, be classed as doubtful.

Tests at 75° and 158° F (no graphs shown) indicate that the rate of relaxation is uniform except for slight breaks in the curves for compounds of natural

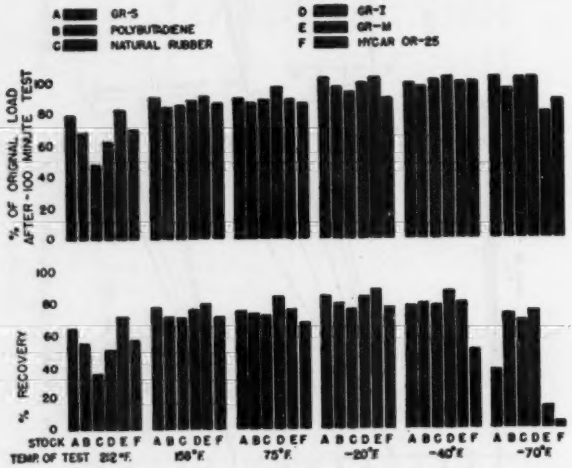

A GR-S
B POLYBUTADIENE
C NATURAL RUBBER
D GR-I
E GR-M
F HYCAR OR-25
% OF ORIGINAL LOAD AFTER 100 MINUTE TEST
% RECOVERY
STOCK A B C D E F A B C D E F A B C D E F A B C D E F A B C D E F A B C D E F
TEMP OF TEST 212°F. 158°F. 75°F. -20°F. -40°F. -70°F.

FIG. 7.—Summary of relaxation and recovery values obtained for the several polymers.

rubber and Butyl rubber after 60 minutes of test. With the possible exception of the Butyl rubber tested at 75° F, these irregularities were of a magnitude that could fall within experimental error. MacDonald and Ushakoff[6] did not report data for any Butyl rubber compounds.

All curves in Figure 3, except that for the "four-hour conditioned" sample of polybutadiene, show uniform relaxation rates for the 100-minute test period at −20° F. After conditioning for 4 and for 24 hours, the specimens of the Hycar compound relaxed rapidly to 44 and 43 per cent of the original loads, respectively.

The stress relaxation experiments at −40° F (Figure 4) show very little change in the applied force when the samples were not conditioned previous to loading. After four hours of conditioning, the Hycar sample was too stiff to be compressed 40 per cent while all the other compounds showed much greater relaxation than when not conditioned. The slight breaks in these lines cannot be explained at present. The spread in percentage of original load of the five

samples after 24 hours of conditioning, was considerably less than that obtained after four hours of aging. Figure 5, stress relaxation at −70° F, showed that Neoprene increased in rate of relaxation approximately one-half hour after compression, and indicates the posibility of crystallization. Definite irregularities may also be noted in the GR-S and natural-rubber curves. Because the test-specimen of GR-S, after four hours of aging at −70° F, was too stiff to be compressed 40 per cent, no further experiments were conducted on aged samples at −70° F. Recent tests, however, have shown that, after one hour of aging at −70° F, polybutadiene made at 122° F requires a deflection of about 34 per cent to produce a stress of 1000 pounds per square inch, compared to 7 per cent for natural rubber, 4 per cent for Butyl rubber, and 3 per cent for GR-S.

In Figure 6, a definite increase of the relaxation rate for the natural-rubber compound is noted, whereas both polybutadiene and GR-S appear to relax evenly over a 70-hour period at −20° F. The discrepancy between the relaxation values of GR-S for the 100-minute test and the 70-hour test cannot be explained satisfactorily. Figure 7 presents a summary of the relaxation and recovery values obtained. At temperatures above −40° F, the recovery values (based on original load and not the relaxed load at 100 minutes) appear to parallel the percentage of original load values after the 100-minute test period. In the temperature range between 158 and −40° F, recovery values for GR-S are equal to, or better than, those of polybutadiene and natural rubber, whereas Butyl rubber is superior to all the other polymer compounds over the full range of 212° to −70° F. The inferiority of the recovery properties of GR-S, Neoprene, and Hycar at −70° F is clearly indicated.

SUMMARY AND CONCLUSIONS

Primarily the purpose of this report is to present information obtained with a newly designed instrument to be used for the determination of low-temperature characteristics of elastomers. The versatility of the instrument affords many variations from the testing procedure employed in obtaining the data reported herein.

REFERENCES

[1] Gehman, Woodford, and Wilkinson, *Ind. Eng. Chem.* **39**, 1109 (1947).
[2] Liska, *Ind. Eng. Chem.* **36**, 40 (1944).
[3] American Society for Testing Materials, "ASTM Standards on Rubber Products," ASTM D395-46T.
[4] Sperberg and Svetlik, *India Rubber World* **124**, 182 (1951).
[5] MacDonald and Ushakoff, *Anal. Chem.* **20**, 713 (1948).
[6] Baldwin-Lima-Hamilton Corp., Philadelphia, Penna.
[7] The Foxboro Co., Foxboro, Mass.

MEASURING WET-GEL STRENGTH OF COAGULANT-DIPPED FILMS. PAPER DIP METHOD *

A. I. MEDALIA

BOSTON UNIVERSITY, BOSTON, MASS.

AND

H. B. TOWNSEND AND H. N. GROVER

GENERAL LATEX AND CHEMICAL CORPORATION, BOSTON, MASS.

In the majority of applications of latex, such as dip goods, foam rubber, and castings, the first step is the formation of a continuous film of rubber in the desired shape. Some form of treatment is used, e.g., chemical coagulation, heating or evaporation, whereby the individual rubber particles of the latex are brought in contact with one another, resulting in the establishment of a continuous latticelike phase of rubber suspended in, or permeated by, a continuous phase of water or serum. This system of two continuous phases is termed a wet gel. The tensile properties of this wet gel are far inferior to those of the dried polymer, and it is universally recognized in the latex industry[1] that the weakness of the wet gel imposes a severe limitation on the applicability of latex.

Despite the interest of the latex industry in the so-called wet gel strength, no adequate method has hitherto appeared by which this property can be measured and characterized. This fact is due primarily to the inherent weakness of the wet gel, which makes it difficult to remove a freshly dipped or coagulated film from the form on which it is cast or dipped. For example, a strip may be coagulant-dipped on a glass slide, but distortion of the film usually takes place when the film is removed from the slide. The film may be cast on mercury, but it is difficult to obtain a film of definite shape in this manner.

In the present method, a latex film is deposited directly on a strip of paper of low wet strength by a coagulant dip process. The film assumes the shape of the paper, which can be made in a dumbbell shape for tensile testing. The moist strip of paper contained between the two layers of wet gel tears readily and so does not affect the measurement of the tensile properties. Owing to the low tensile strength of the wet gel, a testing machine of much greater sensitivity than that ordinarily employed in rubber testing must be used.

By this procedure, it is possible to study the tensile properties of fresh coagulant-dipped latex films. These films can also be carried through various procedures, such as leaching and drying, and the tensile properties can be measured at any stage. When these properties are known, it should be possible for the engineer to treat latex films as materials of construction of known properties, which can be handled on a scientific rather than an empirical basis.

* Reprinted from *Analytical Chemistry*, Vol. 26, No. 4, pages 697–703, April 1954. This paper was presented at the 63rd Meeting of the Division of Rubber Chemistry of the American Chemical Society, Boston, Mass., May 27–29, 1953.

APPARATUS

Many of the tensile tests were performed on a simple homemade apparatus, sketched in Figure 1. The dumbbell-shaped strip, *A*, is clamped between two spring clips, *B* and *C*, and the lower clip is pulled by a nylon cord, *D*, which passes around the pulleys, *E* and *F*, and is attached to the wheel, *G*. The wheel is mounted on the output shaft of a 600 to 1 reduction gear, *H*, which is driven by a governor-controlled motor, *I*.

A standard rate of pull of 20 inches per minute has been used. The force is measured by means of a 2-pound postage scale, *J*, with an attached pointer, *K*,

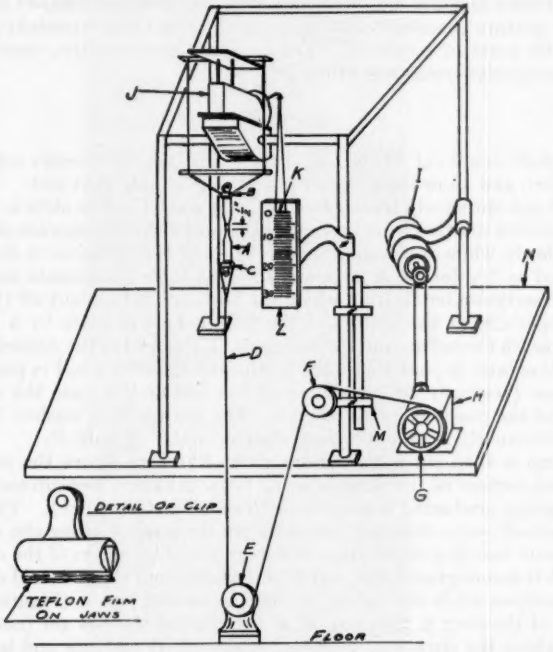


FIG. 1.—Tensile test apparatus.

in front of a scale, *L*, in a position directly behind the strip, *A*. The elongation is measured in the conventional manner by holding a ruler behind the bench marks on strip *A*. The elongation and force at the moment of rupture are noted and recorded. After each strip has been pulled, the position of pulley *F* is adjusted by moving the multiclutch connector[2], *M*; after several strips have been run, cord *D* is unwound and *L* is repositioned. The entire apparatus is mounted on a base plate, *N*.

Other tests were performed on an Instron tensile testing machine[3]. In this machine, the specimen is pulled by a screw mechanism, and the load is measured with a strain gauge connected to a recording potentiometer. In this way complete stress-strain curves are recorded automatically. A ruler is held be-

hind the specimen, and when the bench marks are stretched to a certain length —for example, every inch—a button is pressed which makes a small "pip" on the curve. The Instron machine gives results of much greater sensitivity, precision, and completeness than the homemade instrument. Nevertheless, for laboratories which are unable to purchase an Instron machine, useful results can be obtained with a homemade apparatus.

MATERIALS

The paper employed for this test is Scott toilet tissue, 15 to 20 sheets of which are folded together and cut with a standard dumbbell-shaped die[4]. The coagulant mixture consisted of 40 parts of calcium nitrate pentahydrate dissolved in 60 parts of methanol. The nonionic surface-active agent was an alkyl phenoxypolyoxyethylene ethanol[5].

PROCEDURE

About 0.25 inch is cut off one end of the paper strip (previously cut to shape with the die), and an ordinary paper clip is slipped onto that end. The other end is held in a spring clip similar to clip *B* in Figure 1. The strip is immersed in the coagulant solution for 3 or 4 seconds (until the strip appears saturated), removed slowly while excess solution on the lip of the container is drained off, and allowed to dry for 15 or 20 seconds. It is then hung inside an inverted 4-ounce prescription bottle from which the bottom has been cut off (Figure 2).

The paper clip at the bottom of the strip is held in place by a horseshoe magnet beneath the bottle, and the spring clip is clamped in the desired position. The sample of latex is poured into the bottle, and the strip is left in place for the desired time (generally 30 seconds). At the end of this time the magnet is lowered and the paper strip is removed. The strip is then washed from both sides simultaneously with a stream of distilled water (Figure 3).

The strip is then cut with scissors about 0.25 inch above the paper clip; this severed portion of the strip is saved for a thickness measurement with a thickness gauge graduated in 0.001 inch (Randall and Stickney). The cut end of the dumbbell paper strip is placed between the jaws of spring clip *B* (Figure 1). To avoid handling of the strip, the strip is held by means of the spring clip with which it was originally suspended in the latex, and clip *B* is held open in an inverted position while the end of the strip is lowered into it (Figure 4). The other end of the strip is then cut off at the edge of the wet gel (marking the depth to which the strip was immersed in the latex) and this end is similarly lowered into clamp *C*.

The 0.5-inch bench marks are stamped on the center portion of the strip, using two rubber stamps mounted on tongs so that the lines are marked on the front and back of the strip simultaneously; this is necessary because the strip sometimes turns as it is being pulled so that the front lines may no longer be visible. The motor is then started, and the tensile and elongation are noted as described above and calculated in the conventional manner, i.e., based on the original dimensions of the center portion of the strip.

An alternative dipping procedure is simply to lower the paper strip into a jar of latex. However, the weight of the paper clip is not sufficient to pull the strip down through a fairly viscous latex; furthermore a larger jar and, hence, a larger sample of latex (8 *vs.* 3.5 ounces) is required than in the above method where the strip is held in place in a flat bottle.

Figure 2 Figure 3 Figure 4

FIGS. 2 to 4.—Procedure for dipping, rinsing, and mounting test-specimen.

PROCEDURE FOR DRY FILMS

For the preparation of dry films, a 3 × 8 inch glass slide was dipped in a commercially available calcium nitrate coagulant solution. After partially drying, the slides were dipped for 3 minutes in the latex and then withdrawn. The films were air-dried for 1 hour and then dried for 1 hour in an oven at 58° C. The films were stripped carefully from the slides and lightly dusted with talc. Dumbbell specimens were cut with the die from these films, using the same die as in the wet gel test. These specimens were desiccated 24 hours and were then pulled on either a Scott testing machine or on the Instron machine.

TABLE I

DEPOSITION OF LATEX FILMS

Sample	Solids (%)	Igepal (%)	Gel characteristics	Gel thickness (mils[b])	Elongation at break (%)	Maximum tensile (lb./sq. inch)
			Tensiles Measured on Apparatus in Figure 1[a]			
GR-S-2003	62	—	Good	28	100	25
	62	1	Good	26	1500	22
	40	—	Very soft	—	—	—
	40	1	No film	—	—	—
GR-S-2000	60[c]	—	Soft	—	—	—
	40	—	Good	23	850	21
GR-S-X-667	54[c]	—	Soft, leggy	—	—	—
	54[c]	1	Soft, leggy	—	—	—
	40	—	Good	26	700	15
G-4580[d]	60[c]	—	Good	20	700	45
G-4580[d]	60[c]	1	Good	27	1500	21
G-4794[d]	40	—	Poor	—	—	—
G-4794[d]	40	1	Good	25	2200	15
GR-S-X-710	60	—	No film	—	—	—
	40	—	Good but leggy	21	450	18
Natural (H&C)	62	—	Good	28	900	130
	50	—	Good	26	750	65
	43	—	Good	21	900	60
	62	1	No film	—	—	—
	50	1	No film	—	—	—
	43	1	No film	—	—	—
			Tensiles Measured with Instron Machine			
Natural (H&C)	62	—	Good	25	850	180
	45	—	Good	24	750	57
	32	—	Good	22	720	50
	62[e]	—	Good	19	770	200
	62[f]	—	Good	52	750	200
GR-S-2000(A)	40	—	Good	15	1500	20
	23	—	Good	18	1400	14

[a] All values are averages.
[b] Thickness given is that of the double film of wet gel, corrected for the thickness of paper.
[c] Heat-concentrated.
[d] Experimental low-temperature GR-S latex.
[e] Ten-second dip time.
[f] Three-minute dip time.

RESULTS OF ANALYTICAL SIGNIFICANCE

Film deposition.—In order to be able to carry out a meaningful test, it is first necessary to deposit a good film on the paper. Film deposition on paper appears to be affected by various conditions in much the same way as film deposition on glass or on a metal mold. It is well known in latex technology that many types of latex do not give satisfactory films under any conditions; others require proper adjustment of total solids concentration, or addition of compounding ingredients, to obtain coherent films. The present test serves only to measure the tensile properties of films which can be satisfactorily formed by the coagulant dip process. No standard procedure can be given for the treatment

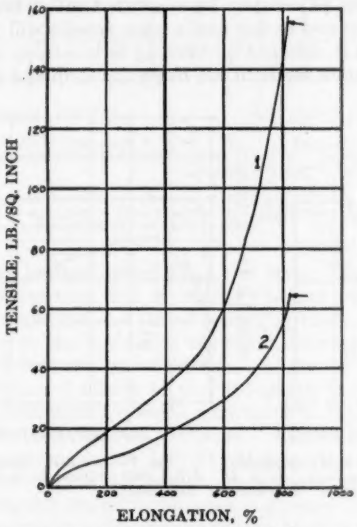


FIG. 5.—Stress-strain curves of natural latex. Arrows indicate point of rupture of specimen.

of the latex prior to film deposition; rather, it is necessary to adjust the concentration and compounding ingredients in the light of experience in order to obtain a suitable film.

Some factors which influence the deposition of GR-S films are illustrated in Table I. A poor film may be obtained if the latex is too dilute; in this case concentration of the latex, e.g., by evaporation, is recommended. On the other hand, if the latex is of high concentration (50 to 60 per cent solids) but is viscous, a soft incompletely coagulated film may be obtained; in this case the latex should be diluted.

If the latex is of a very fine particle size, a very thin film may be obtained which resists penetration by calcium nitrate and so prevents build-up of a film of reasonable thickness; with such a latex the rate of coagulation can be controlled by addition of a nonionic surface active agent, such as Igepal CA-633. However, addition of Igepal to a latex of large particle size (GR-S-2003), which is capable of depositing a good film in the absence of Igepal, results in weakening of the wet gel.

The behavior of natural latex, also illustrated in Table I, is somewhat different from that of the various GR-S samples, in that good films can be obtained from natural latex over a range of the total solids concentrations from 40 to 62 per cent and also in that Igepal prevents deposition of a good film from natural latex. Results obtained with natural latex films at 62 and 40 per cent solids, using the Instron machine, are shown in Figures 5 and 6, in which the tensile is plotted against elongation and jaw separation, respectively. The curves for the 40 per cent solids latex are of similar shape to those of the 62 per cent solids latex, but the tensile values are lower throughout.

Significant results can be obtained only if due care is given to such details as the elimination of bubbles and removal of floc. It is also essential that the calcium nitrate-soaked paper strip be somewhat moist before dipping in the latex; if the salt is allowed to dry out, a poor deposit will result. In practice the desired moistness is obtained by blowing or breathing on the strip. Since the moist calcium nitrate tends to run down the strip and collect on the paper

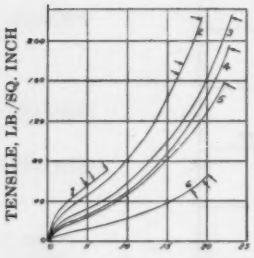


FIG. 6.—1. Neoprene Type 571 (triplicate). 2. Neoprene Type 572 (triplicate). 3, 4, 5. Natural (H & C, 62% solids). 6. Natural (H & C, 40% solids).

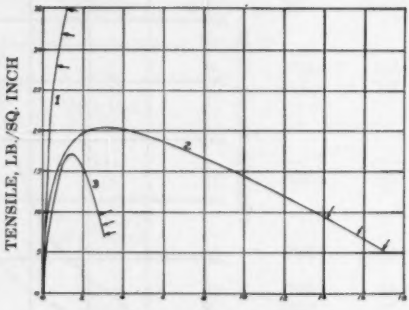


FIG. 7.—1. GR-S 2003 (triplicate). 2. GR-S 2000 (triplicate). 3. Chemigum 235 HS (triplicate).

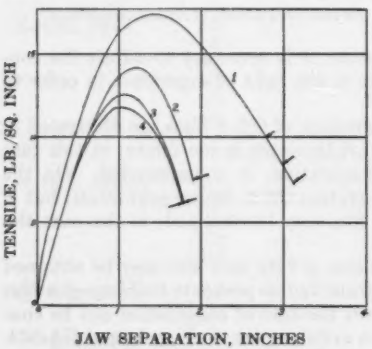


FIG. 8.—Chemigum 235 HS at different rates of jaw separation. 1. 20 inches per minute (triplicate). 2, 3, 4. 5 inches per minute,

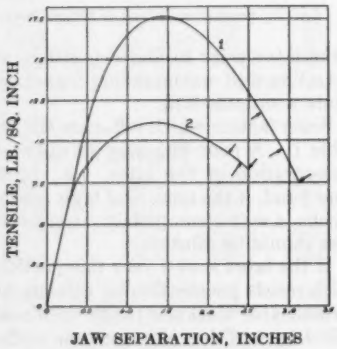


FIG. 9.—1. Chemigum 245 HS. 2. Prevulcanized Chemigum 245 HS.

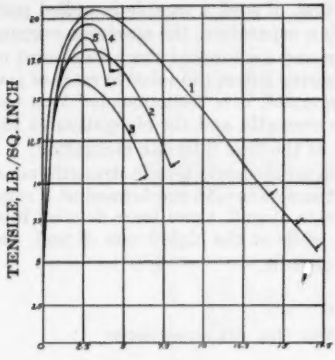


FIG. 10.—1. GR-S-2000(A) (triplicate). 2,3. GR-S-2000(B). 4,5. Prevulcanized GR-S-2000.

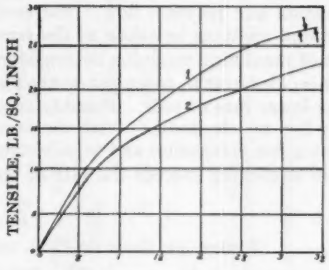


FIG. 11.—Natural latex. 1. Prevulcanized (Type C) (triplicate). 2. Raw (initial portion of curve).

FIGS. 6 to 11.—Tensile stress (modulus) *vs.* jaw separation of various wet gel samples. Arrows indicate points of rupture of individual specimens. Several arrows on a single curve indicate that the several specimens gave virtually identical curves up to the points of rupture.

clip, this clip may be blotted before using this strip. Hanging the strip in a hygrostat before use was tried, but satisfactory results were not obtained.

With latex films deposited and rinsed according to the above standard procedure, the thickness at the bottom of the dumbbell-shaped strip is generally within 0.001 or 0.002 inch of that at the top.

The latex film does not adhere to the wet paper, except by the capillary action of water. Consequently it seems reasonable to assume that the properties of the film are not influenced by the paper. This assumption is difficult to check experimentally, owing to the difficulty of preparing a free latex film.

Rate of pull.—The effect of the rate of pull is shown in Table II. It is important here to distinguish the different types of stress-strain curves found with wet gels. Natural latex characteristically gives a reverse S-shaped curve, with a steep initial portion, followed by a relatively flat portion, followed finally by a more steeply rising portion. Many synthetics give a curve in which the slope decreases continually up to the break point, with the tensile stress increasing up to the moment of rupture. Other synthetics give a curve in which the tensile stress rises to a maximum and then decreases until the break point. These three types of curves are designated as S, N, and U, respectively. Examples of such curves, as determined with the Instron machine are given in Figures 5, 8, and 11, respectively.

The rate of pull has only a negligible effect on the tensile strength and ultimate elongation of the natural latex gel (S curve). With GR-S-2003 (N curve) there is a slight effect on the tensile and a large effect on the elongation. The elongation of this latex is, in any case, very low and not easily measured. With specimens which give a U-type curve, there is a large effect on the tensile strength, and particularly on the elongation. These specimens form "legs" during the pulling (presumably at or somewhat before the point of maximum tensile stress, or yield point); during the subsequent pulling the polymer flows out of the legs into nodules or into the bulk of the specimen.

It has been confirmed experimentally that, if such a sample is pulled past the yield point and is then held at a fixed jaw separation, the specimen eventually ruptures. Accordingly, the elongation and modulus at the break point of such samples are of little significance but merely reflect the relative rates of jaw separation and polymer flow. For such samples, it is recommended that the maximum modulus be taken as the tensile strength, and the elongation at the point of maximum modulus be considered as the true ultimate elongation.

It is of interest to speculate on the reason for the lower tensile strength found at the lower rate of pull. Possibly small tears or breaks are formed at a relatively low tensile stress. With the lower rate of pull, these tears develop into legs at a low elongation and tensile stress, while at the higher rate of pull, the rate of stretching exceeds the rate of tear growth.

TABLE II

EFFECT OF RATE OF PULL ON WET GEL MEASUREMENTS[a]

Sample	Solids (%)	Gel thickness (mils[b])	Rate of pull (inches/min.)	Type of curve[c,d]	Elongation (%) Max.	Elongation (%) Break	Tensile (lb./sq. inch)
Natural (H and C)	62	26	20	S	—	850	180
	62	25	5	S	—	950	180
GR-S-2000 (B)	40	18	20	U	200	530	17
	40	17	5	U	100	290	11
	40	17	1	U	90	150	8.5
GR-S-2003 (B)	62	26	20	N	—	80	24
	62	24	5	N	—	35	19
	62	25	1	N	—	40	16
Prevulcanized Natural	60	27	20	N	—	260	36
	60	27	5	N	—	150	22
Prevulcanized GR-S-2000	40	18	20	U	170	260	20
	40	22	5	U	120	160	12
Chemigum 235 HS	42	23	20	U	—	250	18
	42	23	5	U	—	140	13

[a] All values are averages of three or more runs on the Instron machine.
[b] Double film without paper.
[c] See discussion of rate of pull.
[d] For U curves, elongation given at point of maximum tensile as well as at break point. Tensile given only at its maximum value.

For ordinary work, a rate of pull of 20 inches per minute is recommended in standard testing. This is about as fast a rate as will permit accurate measurement of the elongation. A slower rate is undesirable from the standpoint of tearing, as well as from the practical consideration that an unduly long time would be required to rupture a specimen of high elongation at a slow rate of pull.

RESULTS OF PRACTICAL SIGNIFICANCE

Wet gel strength of raw latexes.—Several commercially available latexes have been evaluated by the procedure given above. These latexes were produced in nature or in a reactor, and concentrated and stabilized by various means, but not otherwise compounded. Results are given in Table III and Figures 5 to 10.

The data of Table III show the great superiority of natural latex over the butadiene-based copolymers in the tensile strength of the wet gel. Neoprene Types 571 and 735 are intermediate between these two extremes; Neoprene

TABLE III

WET GEL STRENGTHS OF RAW LATEX FILMS[a]

Sample	Method of concn.	Wet gel properties: Solids (%)	Gel thickness (mils[b])	Type of curve[c]	Elongation (%): Max.[d]	Elongation (%): Break	Tensile (lb./sq. inch[d])	Dry film properties: 800% modulus	Elongation at break (%)	Tensile strength (lb./sq. in.)
Natural (H and C)	Centrifuged	62	25	S	—	850	180	1350	1200	2650
Natural (NC-401)	Creamed	63	25	S	—	850	160	500	1175	2100
Neoprene Type 571	—	40	21	N	—	450	72	100	1075	1175
Neoprene Type 571	Heat	51	21	N	—	350	75	—	—	—
Neoprene Type 572	—	53	23	S	—	800	190	100	1200	1550
Neoprene Type 735	—	37	19	S	—	2600[e]	110[e]	—	2000[e]	320[e]
GR-S-2000 (A)[f]	—	40	15	U	400	1500	20	—	—	—
GR-S-2000 (B)[f]	—	40	18	U	200	530	17	170	880	180
GR-S-2000	Creamed	53	15	U	90	200	19	—	—	—
GR-S-2001	—	39	11	U	80	2200	13	Film too soft	—	—
GR-S-2003 (A)	—	62	23	N	—	105	36	Film tore too readily	—	—
GR-S-X-710	—	40	21	U	40	1000	18	—	2900[e]	140[e]
GR-S-X-736[h]	—	35	21	U	30	700	14	—	—	—
Chemigum 245HS	Creamed	37	18	U	75	200	19	70	1400	110
Chemigum 235HS	Creamed	42	23	U	50	250	18	—	—	—

[a] All wet-gel values are averages of three or more runs on Instron Machine at a rate of pull of 20 inches per minute.
[b] Double film without paper.
[c] S refers to curves similar to that of Figure 5, N to Figure 11, and U to Figure 8.
[d] For U curves, elongation is given at point of maximum tensile as well as at break point. Tensile is given only at its maximum value.
[e] Elongation of sample too great to permit measurement of conventional dumbbell specimen in Instron machine; therefore straight strips 0.25 × 1 inch were used.
[f] Two different lots.
[g] Owing to extremely high elongation, samples were pulled by hand at approximately 50 inches per minute.
[h] A high-modulus cold GR-S latex, normally oil-extended and coagulated and processed; however, this sample obtained without added oil.

Type 572 is slightly higher than natural latex. Neoprene Type 572 is known to crystallize more readily than Neoprene Type 571. The extremely high elongation of Neoprene Type 735 is worth noting; this is not a false effect caused by "legginess", since the load continued to increase up to the break point.

Most of the butadiene-based copolymers, on the other hand, gave U type stress-strain curves, i.e., curves which rose to a maximum (yield point) and then decreased gradually before the final rupture. Among these copolymers, only GR-S-2003 exhibits a stress-strain curve of "normal" (N) appearance, i.e., rising with continually decreasing slope to a maximum value at the break point, and only this latex gives a tensile strength superior to the other butadiene-based copolymers. However, on the basis of the "tensile product", or tensile strength based on the cross-sectional area at the moment of measurement[6], GR-S-2003 appears comparable to GR-S-2000. There is little to choose between the remaining GR-S-latexes and the butadiene-acrylonitrile latexes (Chemigum 245-HS and 235-HS), regarding tensile strength of the wet gel.

The tensile strength of the natural latex wet gel is about 7 per cent of that of the dry film; for the GR-S and Chemigums the ratio is about 12 per cent. Evidently the low tensile strengths of the latter stocks are to be ascribed to the polymer properties rather than on colloidal properties of the wet gel, or else on colloidal properties which persist in the dry coagulant-dipped film.

The tensile strengths of the various raw latexes are in the same general order as the utilization experience with these latexes, particularly with respect to dipping properties. It is, therefore, proposed that the term "wet gel strength" be defined as the tensile strength of a latex film determined by the above method, or alternatively, that the term "wet gel strength" remain undefined and the term "wet gel tensile" be used for the tensile strength determined above.

Many samples gave films which were unsatisfactory for testing; these included GR-S-X-667 and X-633 (soft and leggy) and two high styrene latexes (Pliolite-160 and Koppers KB-900-A) as well as a polybutadiene latex (GR-S-X-653), all of which were crumbly.

Wet gel strength of prevulcanized latexes.—For various applications it is common to use prevulcanized latex, either natural or synthetic. Wet-gel properties of several prevulcanized latexes are shown in Table IV and Figures 9 to 11.

It is seen that the tensile strengths and elongations of the prevulcanized natural latex wet gels are considerably lower than those of the natural latex from which they were prepared. Both tensile strength and elongation decrease with increasing degree of cure. Evidently as the rubber within each polymer particle becomes more cross-linked, the individual polymer particles become less cohesive.

It is of particular interest to compare the shapes of the stress-strain curves obtained with raw and prevulcanized latex samples. Prevulcanization of natural-rubber latex causes little change of the intial portion of the curve, but the final rising portion obtained with raw natural latex is completely absent in the prevulcanized stock. This final rising portion is presumably due to alignment of molecules to form crystallites. In order for this alignment to take place before rupture of the specimen, it would seem essential that molecules from adjacent latex particles come in contact with one another and share in crystallite formation. Prevulcanization introduces cross-links within each particle and restricts the freedom of motion of the molecules within each particle, so that molecules from adjacent particles may not be able to align with one another.

In the dry film, on the other hand, some cross-linking has taken place be-

TABLE IV

WET GEL STRENGTH OF PREVULCANIZED LATEX FILMS[a]

			Wet gel properties					Dry film properties			
Sample	Base stock	Solids (%)	Gel thickness (mils[b])	Type of curve	Elongation (%) Max.	Elongation (%) Break	Tensile (lb./sq. inch)	*T*-50 (° C)	600% modulus	Elongation at break (%)	Tensile strength (lb./sq. in.)
A	Natural	62	23	N-S	—	550	30	13.5	300	1070	3600
B	Natural	62	23	N	—	250	45	12.2	600	1040	5700
C	Natural	62	26	N	—	310	51	12.0	650	960	4600
D	Natural	62	26	N	—	200	28	9.0	1100	880	5175
E	Natural	62	27	N	—	100	22	7.0	875	870	4575
F	GR-S-2000	40	18	U	170	260	20	—	800	710	1400
G	Chemigum 245	43	19	U	75	200	11	—	—	1150	<100

[a] All wet gel values are averages of three or more runs on Instron machine at a rate of pull of 20 inches per minute.
[b] Double film, without paper.

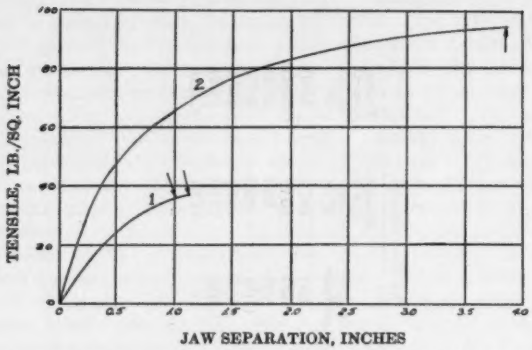


FIG. 12.—Comparison of wet gel and partially dried GR-S-2003 film. 1. GR-S-2003 wet gel. 2. GR-S-2003, dried 10 minutes at 105° C.

tween adjacent polymer particles, thus forming a continuous polymer network, with a high tensile strength. There is no apparent correlation between the wet-gel tensile strength and the degree of cure, as indicated by the $T - 50$ value. However, these latexes were prevulcanized according to different types of formulas.

The raw synthetic latexes which gave U curves showed comparatively little change of both the shape of the curves and the actual tensile and elongation values on prevulcanization.

From the practical standpoint, several of the prevulcanized natural latexes show lower tensile strengths than GR-S-2003 (sample A, Table III). It is well known that the dip properties of prevulcanized natural latex are superior to those of GR-S-2003. For example, a dipped doll's foot prepared from the

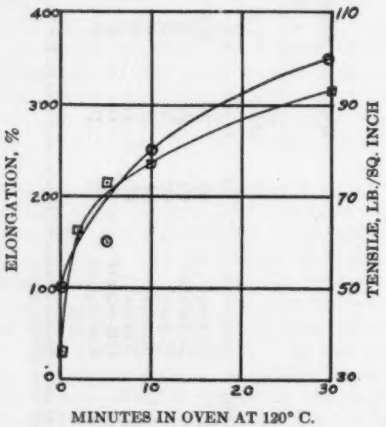


FIG. 13.—Elongation and tensile strengths of GR-S-2003 films dried for various lengths of time.
○. Elongation
□. Tensile strength

former can be removed from the mold, but not if GR-S-2003 is used as the dip stock. This is due to the extremely low elongation of the GR-S-2003 at a low rate of pull (Table II), reflecting the ease with which this sample tears rather than ruptures.

Drying of latex films.—Profound changes of the structure and properties of a latex film take place as the film is dried. Accompanying the loss of moisture there is necessarily a reduction of volume corresponding to the volume percentage of water lost. If the film is constrained to remain constant in one dimension, for example, by the shape of the form or mold, then a certain stress is set up in this dimension; this may be designated as the "set modulus". During drying there also takes place an increase in the tensile strength of the film,

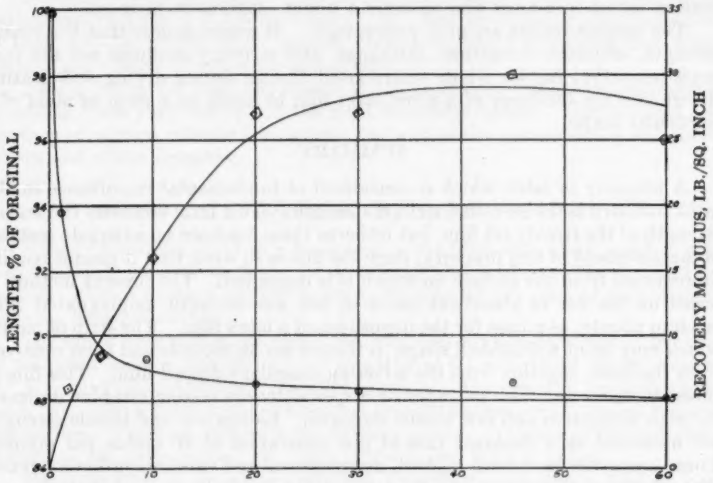


FIG. 14.—Shrinkage and "recovery modulus" of prevulcanized natural latex (Type C) films dried for various lengths of time.

⊙. Length
⊡. Recovery modulus

perhaps by several hundred-fold. An important objective of the present study was to establish relationships between several of the changes which take place on drying under various conditions. Some of the results which were obtained up to the present time are shown in Figures 12 to 14.

Figures 12 and 13 illustrate the change in tensile properties of GR-S-2003 on drying in an air oven (noncirculating). The ultimate tensile strength and elongation values here plotted were obtained with the dumbbell-shaped strips used in the standard procedure given above; after dipping, these strips were dried for the indicated times, then cooled to room temperature and pulled.

To measure the shrinkage of the films on drying, straight strips of toilet paper, 0.5 × 4 inches, were coagulant-dipped by the above procedure, and then one edge of each strip was cut off to permit subsequent removal of the paper. Bench marks were made with India ink at a spacing of 6.50 cm. These strips

were hung in the oven for various lengths of time, then cooled, pressed between glass slides, and remeasured. Each strip so prepared was then stretched to its original length (between bench marks); the tensile stress thus produced, which may be called the "recovery modulus," was measured. As a first approximation, the recovery modulus should be equal to the set modulus, defined above, although the latter should be somewhat the smaller owing to creep during drying.

Values of shrinkage and recovery modulus with a prevulcanized natural latex (sample D of Table IV) are plotted in Figure 14. It is significant that while the shrinkage, or loss of water, is virtually complete in 4 minutes, the recovery modulus has reached only one third of its final value at this stage. In other works, during the heating subsequent to driving off the water, the tension set up in a latex film on a mold would continue to increase.

The present results are only preliminary. It would appear that the tensile strength, ultimate elongation, shrinkage, and recovery modulus are the four most important factors whose interrelated change during drying and heating determines the tendency of a given latex film to break on a form or mold of a particular shape.

SUMMARY

A property of latex which is considered of fundamental importance in the latex industry is the so-called wet gel strength. This term connotes the tensile strength of the freshly set film, but hitherto there has been no adequate method of measurement of this property, since the film is so weak that it cannot readily be removed from the surface on which it is deposited. The present method is based on the use of absorbent paper of low wet strength, impregnated with calcium nitrate, as a base for the deposition of a latex film. The strip of paper, which may be of a dumbbell shape, is dipped for 30 seconds and then removed from the latex, together with the adhering coagulant dipped film. This film is rinsed in water and then mounted on a special tensile testing machine designed for high elongation and low tensile strength. Elongation and tensile strength are measured at a standard rate of jaw separation of 20 inches per minute. These properties have been studied, using natural and various synthetic latexes. The effects of prevulcanization, compounding, and dilution of these latexes have been determined. Tensile properties of the film from a given latex have also been measured as a function of the time and conditions of drying of the film after deposition.

ACKNOWLEDGMENTS

The authors are grateful to the Fabric Research Laboratory of Boston for permission to use the Instron testing machine, and to the General Latex and Chemical Corporation for permission to publish this work. The authors particularly express their appreciation to Dorothy Harrington and Lucy Macali Ronco, who carried out most of the dipping and tensile measurements here reported.

REFERENCES

[1] Zwicker, *Ind. Eng. Chem.* **44**, 774 (1952).
[2] Fisher Scientific Co., No. 14-666-22.
[3] Instron Co., Quincy, Mass., Model TTB.
[4] American Society for Testing Materials, Method D 412-51T, die C.
[5] Ipegal CA-633 of the Antara Chemical Co.
[6] Eaton and Grentham, *J. Soc. Chem. Ind.* (London) **34**, 998 (1915); Maron, Madlow, and Trinastic, *Ind. Eng. Chem.* **40**, 2220 (1948); **44**, 1633 (1952).

POSSIBILITIES IN THE USE OF SODIUM CHLORITE IN LATEX *

(Miss) Josette Tournier

Société d'Electrochimie, d'Electrométallurgie, et des Aciéries Electriques d'Ugine, France

For many years the rubber industry has directed its attention to the oxidation of rubber while in the form of latex. The interesting feature of this process is that it gives latexes which possess notable adhesive properties and which furnish dry rubber which is already plastic.

Among numerous oxidizing agents which have been tested, sodium chlorite is among those that have given the most favorable results. Only a small percentage of sodium chlorite is required, and any excess can be easily eliminated at the end of the operation.

GENERAL PROPERTIES OF SODIUM CHLORITE

Industrial sodium chlorite is marketed in the form of a white powder, with slight greenish yellow reflection. It is perfectly stable when stored dry, and the sodium chlorite content, which is approximately 85 per cent of pure sodium chlorite, does not change.

The salt is very soluble in water, and solutions containing about 30 per cent of technical sodium chlorite can be prepared at 0°, and about 50 per cent at 50° C. Like all such salts, it ionizes in solution. The essential property of the ClO_2^- ion, which is the basis of the most important uses, or at least of the best known uses, of sodium chlorite is its oxidizing power. This is a function of three variables: the temperature, the concentration, and the pH value.

Measurements of oxidation-reduction potentials have shown that, in cold alkaline solution, sodium chlorite has a very mild oxidizing action. But at pH values lower than 4, its oxidizing power becomes very strong, and evolution of chlorine peroxide is observed, probably formed by oxidation of the ClO_2^- ion.

However, the oxidation reaction can be carried out at pH values as high as 7 if an activator of decomposition of sodium chlorite is utilized. This activator can be a reducing agent, e.g., formaldehyde, which decomposes sodium chlorite, for the most part into chlorine dioxide.

In brief, chlorites have the advantage that they can be employed at various pH values and are essentially oxidizing agents. These properties differentiate them from hypochlorites in particular, which tend to function as chlorination agents.

TESTING METHODS

To study the action of sodium chlorite on natural-rubber latex, a centrifuged latex, of 60–62 per cent concentration, and obtained from Indochina, was utilized. Its physical-chemical characteristics are exemplified by its total-

* Translated for Rubber Chemistry and Technology from the *Revue Générale du Caoutchouc*, Vol. 31, No. 1, pages 46–48, January 1954. This paper was presented at the rubber session of the 26th Congress of Industrial Chemistry, Paris, June 1953.

solids content 61.5 per cent, dry-rubber content 59.7 per cent, free-ammonia content 0.7 per cent, pH value 10.3, and Mooney viscosity of sheet rubber obtained by evaporation 130.

The tests which are described below were made on neutral and acidic latexes, initially stabilized by addition of an anionic sufonated compound in an amount equivalent to about 2 per cent of the dry-rubber content. After the chlorite was added to the latex, the mixtures were heated without agitation until the chlorite was completely decomposed when the conditions made this possible. To follow the degradation of the rubber globules, these were isolated by drying at 20° C or by coagulation. The plasticizing effect was judged by measuring

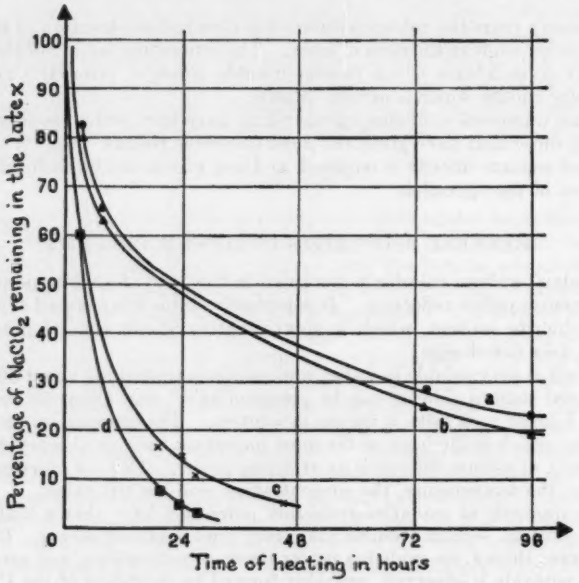


FIG. 1.—Influence of the temperature on the decomposition of sodium chlorite in solution in latex, with the system acidic, and with no formaldehyde present. Temperature 40° C, pH 3.3–4: Curve a, 3.3% sodium chlorite. Curve b, 1.7% sodium chlorite. Temperature 60° C, pH 3.3–4: Curve c, 3.3% sodium chlorite. Curve d, 1.7% sodium chlorite. The percentage of sodium chlorite is based on the dry-rubber content.

the Mooney consistency at 100° C by the consistomer of the French Rubber Institute.

The action of sodium chlorite was studied under two conditions: (1) with the pH value of the medium at 3–4, and (2) with the pH value at 7 and with formaldehyde present.

CHLORITE–ACID PROCESS

To obtain as complete decomposition of the sodium chlorite as possible, the process must be carried out under carefully chosen conditions of temperature and pH value of the medium.

The curves, a, b, c, and d, of Figure 1, obtained by plotting the time as abscissa and the percentage of sodium chlorite as ordinate, show that the process

must be carried out at 60° C; otherwise the rate of decomposition of the chlorite is too slow.

The most favorable results were obtained with the pH value in the neighborhood of 3.

In this process, it is advantageous to add a reducing agent at the end of the reaction to destroy traces of sodium chlorite still present in the latex, even after 48 hours of heating at 60° C. In this way, further reactions during drying of the degraded latex are avoided. (The method of determination of chlorite in latex is described in Appendix 1).

CHLORITE–FORMALDEHYDE PROCESS

The use of sodium chlorite with the pH value of the system at 7 necessitates the presence of a reducing agent, which promotes the formation of chlorine

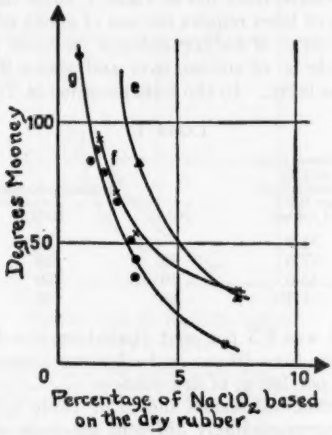


FIG. 2.—Mooney consistency as a function of the temperature of the reaction. Curve e, 20–25° C. Curve f, 60° C. Curve g, 20–25° C with air bubbled through the mixture. The tests were carried out with 50 cc. of 10% formaldehyde per 100 g. of dry rubber.

dioxide. Formaldehyde was chosen as the reducing agent, which makes possible both neutralization of the ammonia and decomposition of the sodium chlorite.

With the time of the reaction fixed at seventeen hours, three factors were studied, viz., the temperature, the concentration of sodium chlorite, and the concentration of formaldehyde.

INFLUENCE OF THE CONCENTRATION OF THE SODIUM CHLORITE AND OF THE TEMPERATURE

As the three curves e, f, and g in Figure 2 show, the plasticity of rubber increases with increase of the concentration of sodium chlorite. Furthermore, an elevation of temperature increases the activity of the sodium chlorite.

Nevertheless, if a sufficiently high proportion of sodium chlorite is used, the oxidation reaction can be carried out at room temperature. Degradation of the rubber is also favored by bubbling air through the latex.

INFLUENCE OF THE CONCENTRATION OF FORMALDEHYDE

The purpose of adding formaldehyde to latex is to neutralize the ammonia and to decompose any sodium chlorite present.

The amount of formaldehyde necessary to neutralize the ammonia is invariable for a given latex; on the contrary, the amount necessary to decompose the sodium chlorite is variable, and depends principally on the amount of sodium chlorite originally added to the latex. The amount of formaldehyde should be sufficiently high so that the rate of transformation of the sodium chlorite in the latex is not too slow, and, at the same time, the amount should not be excessive, for then an important share of the oxidizing power of the sodium chlorite is consumed in oxidizing the formaldehyde.

For the purpose of establishing the optimum amount of formaldehyde, tests were made with a fixed amount of sodium chlorite, but different amounts of formaldehyde. The results, recorded in Table 1, show that the optimum conditions for degradation of latex require the use of about 60 cc. of formaldehyde (330 g. per liter) per 100 g. of sodium chlorite (test no. 2 in Table 1). This amount of formaldehyde is, of course, over and above the amount necessary for neutralization of the latex. In the tests recorded in Table 1, the amount of

TABLE 1

Test no.	Volume (cc.) of 10% formaldehyde per 100 g. of rubber	Mooney consistency		
		20° C	40° C	60° C
1	34.9	—	54	25
2	37.5	85	46	18
3	43.0	80	50	25
4	51.4	88	50	40

sodium chlorite added was 3.3 per cent (based on the dry rubber), and the amount of formaldehyde (as a 10 per cent solution) necessary to neutralize the ammonia was 31.6 cc. per 100 g. of dry rubber.

Based on the experimental results shown in Table 1, different amounts of sodium chlorite and correspondingly different amounts of formaldehyde were added to latex to maintain constant the ratio of formaldehyde to sodium chlorite.

The results of these further tests are shown by the curve i of Figure 3.

Curve h in Figure 3 represents tests made with the same concentration of formaldehyde in all cases. A comparison of these two curves shows the importance of adding the calculated amount of formaldehyde proportional to the amount of sodium chlorite added.

In these tests, it was found that, at the termination of the reaction, no sodium chlorite was present in the reaction mixture, so any further changes during drying of the degraded latex were avoided. The method of determining the chlorite in the latex is described in Appendix 1 and the method of determining formaldehyde in Appendix 2.

DEGRADATION OF LATEX BY SODIUM CHLORITE

PREPARATION OF SOFTENED RUBBER

Degradation in an acid medium.—To 100 g. of stabilized latex hydrochloric acid is added until the pH value of the mixture is 3–4, and then 2 g. of sodium chlorite is added. The mixture is heated 48 hours at 60° C, and any trace of re-

maining oxidizing agent is destroyed by addition of formaldehyde for the purpose of preventing any changes of quality during the subsequent drying process.

Degradation in a neutral medium.—One hundred g. of latex is first stabilized by addition of an anionic compound, then 2 g. of sodium chlorite and 5 cc. of 40 per cent formaldehyde are added for the purpose of neutralizing any ammonia present in the latex and of activating decomposition of the sodium chlorite. The mixture, the pH value of which is approximately 6, is heated 17 hours at 60° C. The oxidized product, dried at 20° C, yields a softened rubber.

In both cases, i.e., degradation in an acid medium and in a neutral medium, the Mooney consistency, measured by the method of the French Rubber Institute, was found to be 20° C.

Rubber prepared by the sodium chlorite-acid process is white; that prepared by the chlorite-formaldehyde process is colored.

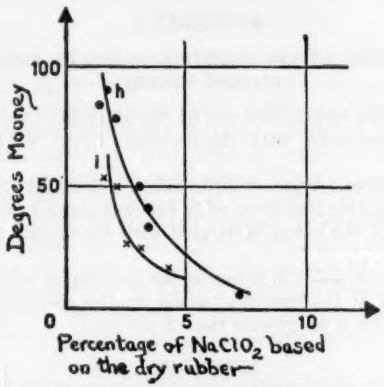


FIG. 3.—Influence of formaldehyde on the Mooney consistency at 60° C. Curve h, concentration of formaldehyde invariable irrespective of the concentration of sodium chlorite. Curve i, concentration of both formaldehyde and sodium chlorite variable. Ratio of formaldehyde to sodium chlorite 60/100 (formaldehyde 330 g. per liter).

In the experiments described, Vulcastab-LS was employed as the stabilizing agent.

GENERAL CONCLUSIONS

The sodium chlorite-acid process and the chlorite-formaldehyde process give dry rubbers which are of almost the same plasticity, but, whereas rubber prepared by the chlorite-acid process is white, rubber prepared by the chlorite formaldehyde process is highly colored.

Both processes plasticize the rubber in latex form, and the small amount of sodium chlorite required means that the processes should be industrially profitable.

SUMMARY

The oxidation of rubber by sodium chlorite can be accomplished either with rubber in the solid form or with rubber in aqueous suspension. The first process gives highly oxidized and very sticky rubbers. By the second process, the oxidation can be controlled so that all the sodium chlorite is decomposed in the latex, i.e., before coagulation and drying.

The decomposition reaction is carried out either in neutral medium in the presence of an activator of decomposition of the sodium chlorite, e.g., formaldehyde, or in an acid medium with pH between 3 and 4.

The oxidation process, which requires only small percentages of sodium chlorite, can be adapted to the manufacture of adhesive from latex and the preparation of rubbers plasticized directly without mastication.

These degraded latexes react easily with various reactive agents of normal rubber, in particular with halogens.

ACKNOWLEDGMENT

The author expresses her appreciation to the French Rubber Institute for the material aid which was generously accorded her in carrying out the experiments and for suggestions offered during the course of the work.

APPENDIX 1

DETERMINATION OF THE OXIDIZING POWER OF LATEX–SODIUM CHLORITE MIXTURES

This determination was carried out by the iodometric method, in weak acid medium, and in accordance with the reaction: $ClO_2^- + 4H + 4I^- \rightarrow Cl^- + 2H_2O + 2I_2$.

To 10 g. of the latex-sodium chlorite mixture is added 15 cc. of 10 per cent aqueous potassium iodide and 15 cc. of 30 per cent acetic acid, the mixture is let stand 3 minutes, and the iodine is titrated with decinormal sodium thiosulfate solution.

The results are expressed in terms of the percentage of sodium chlorite remaining at the end of the reaction, based on the sodium chlorite originally added. The precision is no greater than 3 per cent.

APPENDIX 2

DETERMINATION OF 10 PER CENT FORMALDEHYDE SOLUTIONS

By the action of hydroxylamine hydrochloride on an aldehyde, an oxime is formed, with liberation of hydrogen chloride, thus: $HCHO + NH_2OH \cdot HCl \rightarrow H_2C{:}NOH + HCl + H_2O$.

This reaction was utilized in the titration of formaldehyde solutions. Ten cc. of a 5 per cent solution of hydroxylamine hydrochloride and 10 cc. of a 0.1 N solution of formaldehyde are made to react 30 minutes, and the hydrogen chloride liberated is titrated with a 0.1 *N* solution of sodium hydroxide, using bromophenol blue as indicator.

ELECTRON MICROSCOPY OF HEVEA LATEX GELS *

A. J. DE VRIES

RESEARCH DEPARTMENT, RUBBER STICHTING, DELFT, HOLLAND

AND

V. CH. DALITZ

DIVISION OF ELECTRON MICROSCOPY, TECHNICAL PHYSICS DEPARTMENT, T. N. O., DELFT, HOLLAND

INTRODUCTION

The use of preserved concentrated Hevea latex for the production of rubber articles has given birth, during the last decades, to a number of quite new technological methods in rubber manufacture. Starting from an aqueous rubber dispersion of low viscosity as a raw material, instead of the very tough viscoelastic solid rubber, may be advantageous in many respects. Latex technology, however, also presents its particular difficulties and drawbacks, one of which is concerned with the problem of the reinforcement of rubber. Reinforcing fillers like carbon black, which enhance the tear strength and abrasion resistance of masticated rubber, do not exhibit the same beneficial effect on the properties of rubber films cast from latex; the same is true of all fillers if added in appreciable amounts, with the notable exception of resorcinol-formaldehyde resins formed in situ[1]. Nevertheless, the strength of vulcanized cast films from latex is excellent in comparison with vulcanized sheets of masticated solid rubber[2].

In order to get more insight into the factors which control the rheological and mechanical properties of wet as well as dried and vulcanized latex gels, an extensive study has been undertaken, part of which has been concerned with an elucidation of the structure of these gels by means of electron microscopy. The purpose of this paper is to describe the experimental methods for obtaining electron micrographs and to present some of the results. The rheological and mechanical properties will be discussed in forthcoming publications, one of which has appeared in print already[3].

EXPERIMENTAL

For the examination of the structure of latex films, the replica technique has been used in our investigations. The same technique has been applied very successfully by Bradford for various synthetic polymer latexes[4]. The rubber film may be formed by casting latex on a glass plate or by simply spreading a droplet of latex directly on a copper object grid. Immediately after formation of the film, the grid is placed in a vacuum chamber and coated with a layer of silicon monoxide (SiO) evaporated from a molybdenum boat. The hydrogen containing carbon compound produced by an electrical discharge in toluene vapor may also be used as the replica forming material[5]. In order to obtain a

* Reprinted from the *Transactions of uttithe Instion of the Rubber Industry*, Vol. 30, No. 3, pages 76–80, June 1954. This work is Communication No. 266 of the Rubber-Stichting, Delft, Holland.

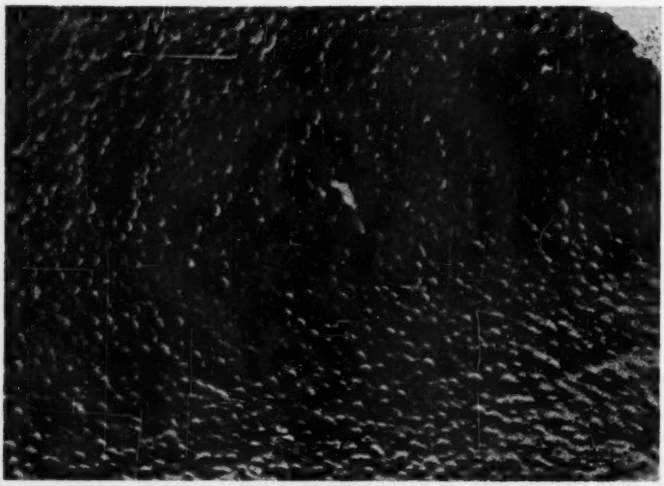


FIG. 1.—Carbon replica of film cast from fractionated Hevea latex on glass. The picture shows some wrinkling of the replica formed during the solubilization of the rubber.

FIG. 2.—Silicon monoxide replica of Hevea latex gel charged with whiting (100 parts by weight on 100 rubber).

distinct picture in the electron microscope, it is necessary to prepare replicas of the gel surface which are perfectly clean and not contaminated by any rubber. A great part of the rubber in Hevea latex is, however, insoluble in any solvent. To overcome this difficulty, the average molecular weight has to be decreased, e.g., by treating the latex with hydrochloric acid and sodium chlorite at room temperature. If the latex has been treated in this way, the rubber can be dissolved very easily in chloroform, leaving a thin layer of silicon monoxide (or carbon) on the specimen grid. If untreated latex is used, the rubber film is made soluble in chloroform by leaving the rubber film covered by the replica

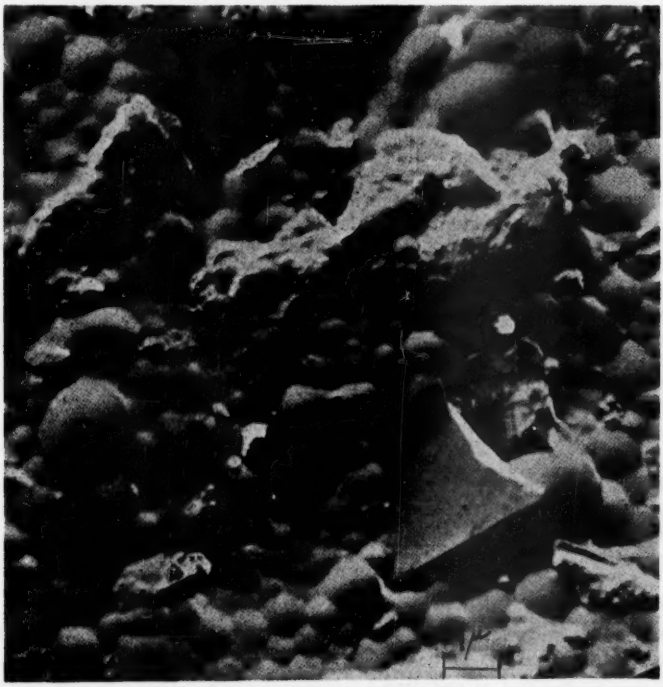


FIG. 3.—Same as Figure 2 but in larger magnification.

in a mixture of hydrochloric acid and sodium chlorite for some hours. If whiting is present in the latex, this filler is to be removed from the replica by a suitable agent, e.g., by dilute hydrochloric acid.

Finally, the replica is caught on the electron microscope specimen screen to be examined and pictured. The replicas appear to show a rather pronounced contrast, and this makes shadow casting unnecessary.

RESULTS AND DISCUSSION

Figure 1 shows a picture of the carbon replica of a film cast from fractionated Hevea latex. Fractionation has been accomplished by creaming[6]. Volume-

average diameter of the rubber globules in this latex is equal to 0.28 micron, measured by electron microscopy[7]. Though the particle size after film formation cannot be estimated very accurately from a replica picture, it is evident that coalescence of the rubber globules has hardly taken place since the average particle diameter in the gel has about the same value as in the original latex. Figures 2 and 3 are pictures of a silicon monoxide replica of a film cast from a mixture of fractionated Hevea latex and a whiting dispersion. The rubber globules in this latex had a volume-average diameter of 0.9 micron; the aqueous whiting dispersion contained no particles larger than 4 microns. The whiting particles are very irregularly shaped in contrast with the rubber particles, which appear like more or less deformed spheres. In this experiment, the latex had been treated beforehand with hydrochloric acid and sodium chlorite in the presence of a nonionic emulsifier. Notwithstanding the partial breakdown of the rubber molecules as a result of this oxidative treatment and the consequent lowering of the viscosity of the polymer, coalescence of the rubber particles during and after film formation has not proceeded to any considerable extent. Coalescence of the rubber globules in a latex gel is not only hampered by the high coefficient of viscosity of the rubber[8], but primarily by the presence of an interfacial layer composed of protein and soaps, surrounding the particles. The influence of the composition of this layer on the rate of coalescence has been established quantitatively[9]. Taking account of the peculiar structure of a latex gel or film in which the original rubber particles have not completely lost their identity, it is clear now why reinforcement of the rubber does not result from mere cocoagulation of a mixture of rubber latex and a filler dispersion: a strong interaction between rubber molecules and filler particles is not attained in this way. However, a thorough knowledge of the structure of latex gels and the factors by which it is controlled may open the way to new methods of improvement and reinforcement of rubber articles made from latex.

ACKNOWLEDGMENT

This work forms part of a program of fundamental research on latex problems undertaken by the Research Department of the Rubber-Stichting, under the management of H. C. J. de Decker.

REFERENCES

[1] Le Bras and Piccini, *Ind. Eng. Chem.* **43**, 381 (1951).
[2] Houwink, de Vries, and van't Wout, *Rev. gén. caoutchouc* **30**, 181, Fig. 1 (1953).
[3] De Vries and van den Tempel, *Proc. Intern. Congr. Rheology*, Oxford 1953, Butterworth, London, 1954, p. 291.
[4] Bradford, *J. Applied Chem.* **23**, 609 (1952).
[5] König and Helwig, *Z. Physik* **129**, 491 (1951).
[6] McGavack, *Ind. Eng. Chem.* **31**, 1509 (1939).
[7] Van den Tempel, *Trans. Inst. Rubber Ind.* **28**, 303 (1952).
[8] Dillon, Matheson, and Bradford, *J. Colloid Sci.* **6**, 108 (1951).
[9] To be published.

DETERMINATION OF PARTICLE-SIZE DISTRIBUTION IN GR-S LATEXES *

ALFRED NISONOFF, W. E. MESSER, AND L. H. HOWLAND

NAUGATUCK CHEMICAL DIVISION, UNITED STATES RUBBER CO., NAUGATUCK, CONNECTICUT

Techniques involving the use of gravitational or centrifugal force have been used for the measurement of particle size and particle-size distribution in a large number of dispersions. Gravitational force is sufficient for the sedimentation of the particles in many suspensions, but the refinements and high speed of the ultracentrifuge are necessary for the analysis of solutions. Centrifuges of moderate speed have been widely employed for analysis of suspensions in which the particles are of intermediate size, especially those in which a fine power is dispersed in a liquid medium. Meadors and Messer[1] showed that the minimum particle diameter in a GR-S latex can be determined in an International Type SB-1 laboratory centrifuge. This indicated the possibility of using this centrifuge to determine particle-size distribution in GR-S latexes.

The principal methods employed with GR-S latexes have been electron microscopy and fractionation with ammonium alginate, followed by the application of electron microscopy[2] or a turbidimetric method[3] to the fractions. Analysis by the proposed method based on Stokes' law requires no very expensive equipment or time-consuming preliminary fractionation; no changes are introduced in the process of measurement except those attributable to a mechanical force acting on the particles; the method can be used to determine the per cent by weight of widely scattered large particles, which are significant because of their weight and for which electron microscopy is not very practical.

The validity of the technique was examined by tests for reproducibility and by comparison with the results of electron and light microscopy. The method was used to determine the particle-size distribution curves of various latexes. Some additional data on latexes in plant production were obtained.

DISCUSSION

In the use of an ordinary centrifuge for an analysis of particle-size distribution in GR-S latex, several advantages appear as a result of the fact that the particles are less dense than the aqueous medium and hence rise in the tube. When a suspension in which the particles descend is centrifuged in a cylindrical vessel, particles are continually striking the walls of the vessel as they move radially outward from the axis of rotation, and they may set up convection currents large enough to introduce appreciable errors[4]. This can be prevented by the use of a specially constructed sector-shaped vessel. However, as GR-S particles migrate toward the axis of rotation and away from the walls of the container, this problem does not arise. Another advantage is the increased centrifugal force available as a result of the upward movement of particles. Since the reference point is the bottom of the tube and since aliquots are removed for analysis from a point near the bottom, the centrifugal force applied to the parti-

* Reprinted from *Analytical Chemistry*, Vol. 26, No. 5, pages 856–861, May 1954.

cles under consideration is about twice as great in the apparatus used in this work as it would be if the top of the centrifuge tube were the reference point, i.e., if the particles migrated away from the axis of rotation.

A third factor is the simplification of the mathematical analysis of data obtained by the pipet technique[5]. When gravitational force alone acts on spherical particles, such as those in GR-S latex, data can correctly be analyzed on the assumption that the fractional loss in solids content at a given point in the vessel, after a measured time interval, corresponds to the weight fraction of dispersed solids consisting of particles larger than a certain calculated diameter, d_c. This diameter is that of a particle which will just reach the point of sampling from the bottom of the vessel (or the top, if particles move downward) during the experiment. The value of d_c can be calculated by Stokes' law from the experimental variables. However, when centrifugation is used, errors are introduced by the convergence of particles as they move radially toward the axis of rotation and by the difference of rates of movement of particles of a given diameter which initially are at different distances from the axis of rotation; a more distant particle will, of course, have a higher average velocity. Both of these factors will have the effect of increasing the concentration of pacticles smaller than d_c at the point of sampling. (This part of the discussion applies to particles less dense than the medium. If the particles move outward in the centrifuge tube, the concentration of particles smaller than d_c will be less at the point of sampling than before centrifuging.) Hence, errors are introduced if one calculates the weight fraction of particles larger than d_c on the assumption that the concentration of smaller particles has not changed. The magnitude of the error caused by these effects depends on the ratio R_1/R_2, where R_1 is the distance from the axis of rotation to the bottom of the centrifuge tube and R_2 is the distance of movement of particles to the point of sampling.

Brown, who gives a mathematical analysis of these factors[6], proposes that the ratio of the length of the centrifuge arm to the distance settled should exceed 2 to 1 if data of sufficient accuracy for control tests are to be obtained. If 50-cc. tubes are used in the Type SB-1 centrifuge and the height of removal of aliquots is limited to a maximum of 2.5 cm., the ratio can be kept above 8 to 1; for most of the present work it exceeded 10 to 1, and errors caused by increased concentration of particles smaller than d_c were necessarily small. This ratio would have been less than one-half as large if the top of the tube were the reference point, i.e., if particles moved outward. In the work of Norton and Speil[7], who constructed a long-arm centrifuge for the purpose of minimizing R_1/R_2, the ratio was about 8 to 1. Their method of analysis was similar to that used in this work, except that concentrations at a given depth were determined by measurement of specific gravity with a hydrometer, rather than by direct determination of solids content.

Stokes' law was used to calculate the particle diameter, d_c, corresponding to the point of sampling. When the centrifuge is used the basic expression takes the form[8]:

$$d_c^2 = \frac{18\,\eta}{\omega^2(\rho - \rho_0)t} \ln \frac{x_2}{x_1}$$

where η is the viscosity; ω is angular velocity; $(\rho - \rho_0)$ is the difference of density between particles and medium; t is the time of centrifuging; x_2 and x_1 are the distances from the axis of rotation to the bottom of the tube and to the point of sampling, respectively. Latex particles over ~20,000 A. in diameter were estimated by allowing them to rise under the influence of gravity. The

centrifuge was used for smaller particle sizes. The lower limit of particle diameter in a typical GR-S latex that can be investigated in 8 hours of centrifuging is about 500 A. This limit can probably be extended by centrifuging for a longer period of time, by using a somewhat more powerful centrifuge, or by adding a suitable soluble material to increase the difference in density.

EXPERIMENTAL

In practice, the value of η is established by diluting the latex with distilled water and testing with a Brookfield viscometer until its viscosity differs from that of water by less than 10 per cent. More water is then added to ensure that this condition is met. The latex is then further diluted to 2 per cent solids. The relative viscosity is taken as 1.05, with a maximum relative error of 5 per cent. This corresponds to a maximum relative error in particle diameter of 2.5 per cent. The density of the polymer is determined by calculation from the density of the latex and that of the clear serum obtained by creaming with ammonium alginate present in a concentration of 0.2 per cent. This concentration of alginate has a negligible effect on the serum density. Also, the volume change on creaming was not detectable in a 100-cc. volumetric flask, which indicates that the densities of serum and polymer are additive. The serum density of the diluted latex is calculated from the original serum density and the extent of dilution. Since it is necessarily very close to that of water, this calculated value cannot be significantly in error. Because of the high dilution, the uncertainty in density of serum will ordinarily be less than 0.0002 unit.

Temperature of the latex on centrifuging is controlled to within $\pm 2°$ C of room temperature by keeping a dry ice-acetone bath in contact with the surface of the centrifuge. Experimentation showed the amount of contact surface necessary at a given rotational speed. The relative error of particle diameter, due to change of viscosity with temperature, is approximately 1 per cent per degree Centigrade at room temperature. In most experiments, 2700 r.p.m., corresponding to a relative centrifugal force of 1510 times gravity, is used. Temperature of the contents is measured after each run and the appropriate viscosity is used in the calculations. Rotational speed is measured with a Waltham tachometer, which was found to agree within 100 r.p.m. with a Jones tachometer at various speeds tested. At 2700 r.p.m. the tachometer was checked against a revolution counter and found to be correct to within 40 r.p.m. The motor of the International Type SB-1 centrifuge used is mounted in rubber, which makes it self-balancing to some extent. Agitation is reduced by filling the 50-cc. centrifuge tubes as completely as possible and by releasing the brushes of the motor when allowing the centrifuge to come to rest. An essentially flat bottom is necessary for use of the pipet technique[5]. This condition is met by putting a few cc. of mercury in the bottom of the centrifuge tube.

After being stirred, the latex is allowed to stand or is centrifuged for a measured period of time, then an 0.8 to 1.0-cc. sample is removed with a hypodermic needle from a level, h, at a measured distance from the bottom of the tube. The needle is moved about to at least five different positions at this level during removal of the sample and is kept at least 1 mm. from the wall. The solids concentration in the sample is determined using an analytical balance. The percentage decrease of solids concentration, compared with the value for the original stirred latex, is taken as the per cent by weight of dispersed solids consisting of particles larger than the calculated d_c (see Discussion). This percentage value must be corrected arithmetically for the per cent solids which do not

migrate, such as electrolyte and shortstop. In most GR-S latexes, all the soap and Daxad is attached to polymer, so that no correction for these components is necessary. The value of d_e is calculated by Stokes' law from the experimental variables. By varying the time of standing or centrifuging, the centrifugal force, and the height from which the sample is removed for analysis of solids content, data are obtained from which the integral weight distribution curve can be constructed. Three points on the curve are usually determined after each period of centrifuging, by analysis of samples removed from three different heights.

The estimated maximum error in the method, obtained by summation of individual errors, is 8 per cent. The probable error, assuming random deviations of errors, is 2.5 per cent. The error can be reduced further by more elaborate measurement of viscosity at some expense of rapidity.

TESTS OF VALIDITY OF METHOD

To test the applicability of the method to very large particles (>100,000 A. in diameter), a sample of X-684[9] containing an unusually high concentration of such particles was used. After the diluted latex had been stirred, samples were removed immediately, and at intervals up to 2 hours, from a point 2.0 cm. above the bottom of the vessel. These samples were placed on a ruled microscope slide of the type used for blood counts and photomicrographs were taken at a magnification of 140×. The use of this type of slide ensures the inspection of a constant volume of latex and the rulings permit direct estimation of particle diameter. As expected, the series of photomicrographs showed a continuous disappearance of the large particles as they passed the 2-cm. mark in their ascent from the bottom of the tube.

For the sake of simplicity, only the first and final photomicrographs are considered quantitatively. In the first, which represents the stirred latex, there were 83 particles larger than 110,000 A. in diameter, 22 of which were over 200,000 A. According to Stokes' law, all particles larger than 110,000 A. in diameter should have risen beyond the 2-cm. mark within 115 minutes, at which time the final sample was removed and photographed. Actually only four such particles remained, the largest of which was about 140,000 A. in diameter. The weight of these four particles, which was calculated from their diameters and known density, was about 0.2 per cent of the total weight of polymer represented by the photograph. Since approximately 10 per cent by weight of the polymer, in that particular sample, was found to consist of particles over 110,000 A. in diameter, the relative error introduced by these four remaining particles was negligible. A few very large particles were observed which were not spherical. However, these were obviously much larger than the 110,000 A. particles and did not interfere with the experiment, since they passed the 2-cm. mark before 115 minutes had elapsed, as expected.

In addition to this experiment, it was necessary to show that there is no decrease of concentration of smaller particles at the 2-cm. mark during the 115-minute interval. To check this assumption, the number of particles between 50,000 and 110,000 A. was counted in a representative area of each of the series of six photomicrographs. Since there is necessarily an appreciable error in measuring the small particle images, the counts were made independently by two observers. The results, representing the photomicrographs taken at intervals during the 115-minute period, were as follows: first observer: 79, 64, 84, 73, 83, 85 particles between 50,000 and 110,000 A.; second observer: 74, 61, 77,

73, 68, 68 particles. The significant fact is the absence of a downward trend. This contrasts with the decrease of the number of particles over 110,000 A. (from 83 to 4) in the same period. It seems very unlikely that there was any decrease at the 2-cm. mark of the number of particles under 50,000 A. in diameter, since these are affected even less by gravitational force. Therefore, within the limits of error of this experiment, the decrease of concentration at the 2-cm. mark must be associated with particles over 110,000 A. in diameter, as predicted by Stokes' law.

Because good reproducibility is an indication of undistrubed movement of particles, it was felt to be of considerable significance. This was an especially important point to investigate in the use of an inexpensive centrifuge, since it was essential to prove that agitation and convection currents did not introduce errors. Duplicate determinations of solids content, at the same height of sampling, have been made in 152 cases after centrifuging duplicate samples of diluted GR-S latexes. The mean deviation was calculated for each pair of

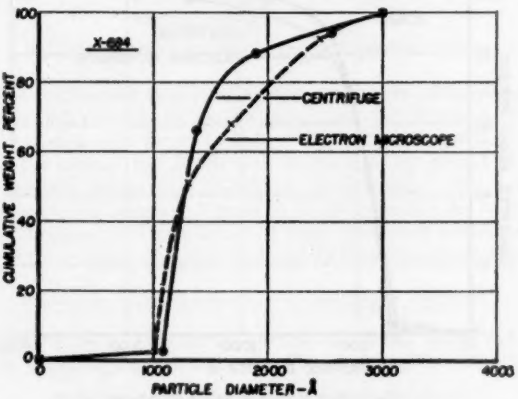


FIG. 1.—Comparison of integral weight distribution curves.

results. The arithmetic mean of all values of mean deviation is 0.23 mg. per gram. At an initial concentration of 2 per cent (20 mg. per gram) this corresponds to 1.2 per cent of the total polymer. Since values for the weight per cent over d_c are based on the total weight of polymer, the value 1.2 per cent is a measure of the precision of data plotted in the integral weight distribution curves.

As another check of the validity and reproducibility of the method, ten replicate samples of diluted X-684-type latex were centrifuged at 2700 r.p.m. in five separate runs. In each case, a sharp boundary was obtained between the latex and a transparent serum below. Minimum paritcle diameter was calculated by Stokes' law from the height of this boundary. The mean value was 1090 A, with a mean deviation of 30 A. and a maximum deviation of 50 A. This agrees very well with electron photomicrographs of the same latex, which show a large number of particles 1010 to 1050 A. in diameter, but a very few scattered particles under 1010 A. (less than 2 per cent of the total weight of polymer). [Measured diameters were divided by the factor 1.096 to correct

for the swelling of particles on bromination[19]]. In addition, solids concentration was determined in eight of the ten replicate experiments described on samples removed from a point corresponding to d_e = 1900 A. The mean relative decrease of solids, compared with the original value, was 19.3 per cent with a mean deviation of 1.2 per cent and a maximum deviation of 2.2 per cent. Serum-to-latex boundaries also have been obtained by centrifuging duplicate samples of over 30 different latexes produced in the pilot plant and plant. In almost every case, the heights of these boundaries were found to agree within 1 mm. If the boundary height is 1 cm. (a typical value), a difference of 1 mm. corresponds to a relative difference of 5 per cent in the minimum particle diameter. These examples of reproducibility afford additional evidence of undisturbed movement of particles.

A comparison of particle-size distribution curves for two latexes, obtained by centrifugation and electron microscopy, is shown in Figures 1 to 4. Data

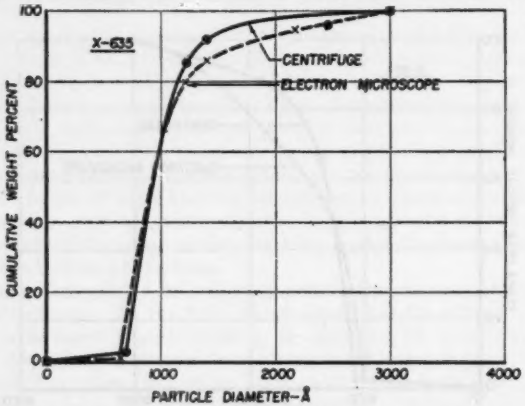


FIG. 2.—Comparison of integral weight distribution curves.

obtained in the centrifuge yield an integral weight distribution curve. This type of curve was obtained from the electron photomicrographs by measuring particle images and weighting each particle in proportion to the cube of the diameter. Although approximately 2000 particles of each latex were measured, so few particles over 3000 A. in diameter were present in the photographs that they could not be considered as representative. Therefore, for purpose of comparison, it was necessary to normalize the curves obtained by both methods so as to represent 3000 A. as the maximum diameter. Obviously, this has very little effect on the differential number distribution curves. The latter were obtained from the photomicrographs by direct measurement of particle images, and from centrifugal data by calculation from the integral weight distribution curves. To do this, the relative weight frequency was first obtained in the usual manner by measuring the slope of the integral weight curve. The relative weight frequency at any given point was converted to relative number frequency by dividing by the cube of the diameter. The agreement between the curves obtained by the two methods, as well as the evidence that the movement of particles is reproducible, support the applicability of the technique.

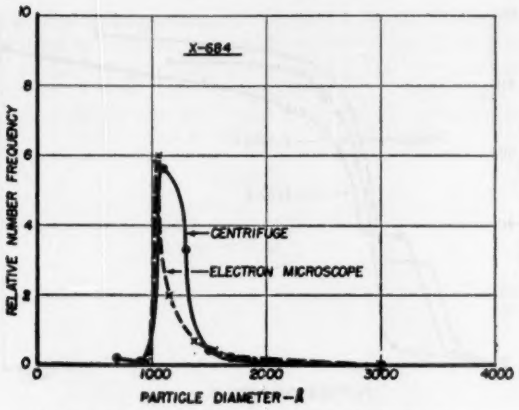


FIG. 3.—Comparison of differential number distribution curves.

It should be emphasized that 3000 A. was not the maximum diameter found in these latexes; 9.2 per cent of the weight of polymer in the X-684 and 16.5 per cent in the X-635 were found to consist of particles larger than 3000 A. in diameter; 1.8 per cent of the X-684 and 14 per cent by weight of the X-635 consisted of particles larger than 100,000 A. in diameter. The method has a lower limit of particle diameters, depending on the power of the centrifuge, but, for practical purposes, no upper limit. Larger diameters are investigated by reducing the time or speed of centrifuging or by using gravitational settling.

DISTRIBUTION CURVES OF OTHER LATEXES

The integral weight distribution curves of several other GR-S latexes, determined by centrifuging, are shown in Figures 5 and 6, where 87 to 95 per

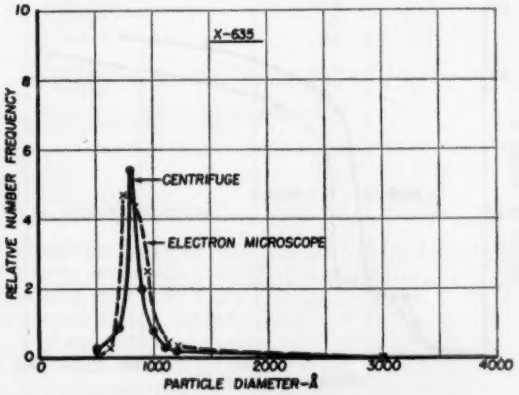


FIG. 4.—Comparison of differential number distribution curves.

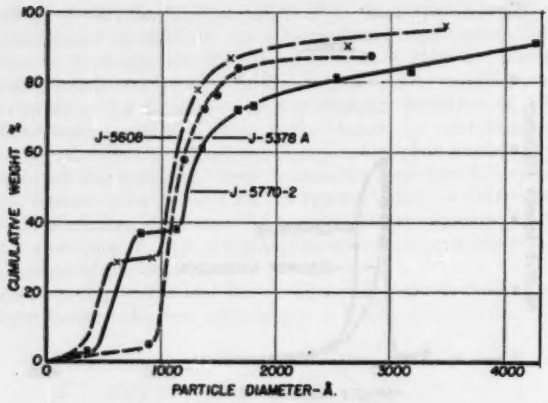


FIG. 5.—Integral weight distribution curves.

cent of the total weight of each polymer is represented. The remaining percentage consists of larger particles, i.e., over 4000 A. in diameter. However, less than 1 per cent of the total weight in each case was over 30,000 A. in diameter, i.e., the self-creaming tendency of these latexes is low. Thus the percentage not represented on the graph consists almost entirely of particles between 4000 and 30,000 A. in diameter. In Figure 5, J-5378-A is a Type X-684 latex with part of the potassium sulfate replaced by potassium pyrophosphate. Its distribution curve is very similar to that of X-684 (Figure 1), but the first abrupt change of slope in the curve, which corresponds essentially to the minimum particle size, occurs at a particle diameter about 100 A. lower than that of X-684. Each of the remaining four latexes in Figures 5 and 6 is more polydisperse than is typical of a high solids latex, since each contains considerable amounts of polymer (18 to 35 per cent by weight) consisting of particles smaller

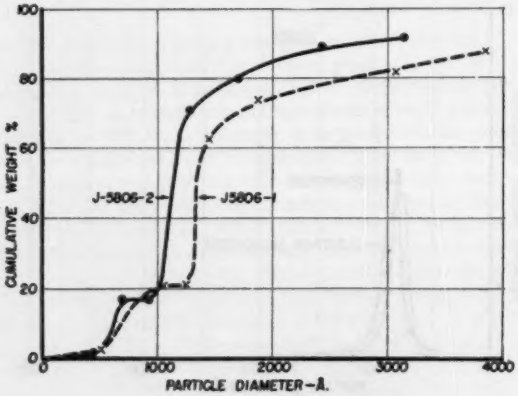


FIG. 6.—Integral weight distribution curves.

in diameter than that corresponding to the abrupt change of slope; as a result there is less polymer in a narrow range of diameters immediately following this change. (Diisopropylbenzene hydroperoxide was the catalyst used in the preparation of each of these four high-solids latexes. J-5608 was made with Dresinate 214 as emulsifier and hydrazine as activator; a feature was the absence of Daxad. J-5806-1 and J-5806-2 are duplicate latexes made with 2

TABLE I

PARTICLE SIZE MEASUREMENTS ON VARIOUS LATEXES IN PLANT PRODUCTION
(February–July 1952)

Type[a]	Code	Butadiene/styrene charging ratio	Wt. % above 100,000 A. in diameter	Wt. % between 4000-100,000 A. in diameter	Av. Diameter below 4000 A.[b]
X-695[c]	602 UC	73/27	0	0.6	910
GR-S-2000[d]	203 UA	50/50	0	0	1260
	217 UC		0	0	1230
GR-S 2002[e]	219 UB	55/45	0	0	1210
	317 UA		0.8	0	1190
	416 UB		0	—	—
	527 UA		0.4	—	—
X-619[11]	501 UC	70/30	5.0	5.4	2010
	511 UA		3.8	9.3	—
	522 UB		3.5	3.7	1790
	529 UA		5.0	8.1	1530
	606 UA		4.8	2.9	1770
GR-S 2100[f]	510 UA	70/30	8.6	0.9	—
	526 UA		7.2	4.2	1550
	530		9.1	4.5	1560
	530 UB		12.6	0.8	1530
X-684[g]	415 UA	70/30	5.0	5.6	1780
	420 UB		2.4	6.1	2130
	422 UA		2.1	8.2	2070
	505 UA		0.7	5.7	1950
	J-5378-A[g]		3.5	7.6	—
	J-5000-C[g]		1.8	2.5	1860
	J-5000-E		9.8	4.4	1790
X-635[12]	J-4248-K[h]	70/30	14.0	—	—
	J-4845-C[g]		4.0	0	1680

[a] First three latexes polymerized at 50° C; remainder at 5° C.
[b] Determined by measurement of total turbidity[3].
[c] Formerly Type II.
[d] Formerly Type IV.
[e] Formerly Type X-446[13].
[f] Formerly Type X-547[14].
[g] Produced in pilot plant.
[h] Type X-635 with increased Mooney viscosity.

parts Neo-Fat K-242 per hundred monomers as emulsifier and activated by sodium formaldehyde sulfoxylate. J-5770-2 is similar to J-5806-1, with the major difference that only 1.25 parts of soap were used.) In the case of J-5770-2, there are two abrupt changes of slope, at 360 and at 1130 A. These four latexes were of especial interest, since each was unusually fluid when concentrated to a high solids content (62 to 66 per cent). It is suggested that this high fluidity is related to the relatively wide distribution of particles sizes, since broader distribution permits closer packing of particles.

The distribution curves of J-5806-1 and J-5806-2 differ mainly in that the first large body of particles appears at a diameter of 1250 A. in the former and at 930 A. in the latter latex. This indicates that there are many more particles in J-5806-2 and agrees with the considerably faster initial reaction rate observed in the polymerization of that latex.

DATA ON LATEXES IN PLANT PRODUCTION

The results of some measurements on latexes in production are given in Table I. The first three types listed are made at higher temperatures (110° to 130° F), while the remainder are examples of cold, high-solids latexes (41° to 50° F). The percent by weight of each latex consisting of very large particles (fourth column, Table I) is a measure of the creaming tendency of the latex, since only such particles rise at an appreciable rate under the influence of gravity. It is evident that the fraction of polymer consisting of such particles is negligible in the hot latexes, but is appreciable in each of the cold high-solids latexes tested. The high values obtained for GR-S 2100 and J-4248-K are in accord with the rather large amounts of cream observed to form in these latexes. The data in the last column confirm the usual findings[15] of large average particle size in cold high-solids latexes. The data were obtained by centrifuging the diluted latex and determining average particle size by measurement of turbidity[3] on a sample removed from a point in the centrifuge tube such that particles larger than 4000 A. in diameter were absent.

SUMMARY

A method based on Stokes' law, involving the use of an ordinary laboratory centrifuge, is described for the determination of particle size distribution in GR-S latexes. It is shown to be valid by tests for reproducibility and by comparison with the results of light and electron microscopy. In applying the method, several unusually fluid high-solids latexes made in the pilot plant were found to be characterized by a wide distribution of particle sizes. Data on various latexes in plant production are reported.

ACKNOWLEDGMENT

This work was performed as a part of the research project sponsored by Reconstruction Finance Corp., Office of Synthetic Rubber, in connection with the Government Synthetic Rubber Program.

REFERENCES

[1] Meadors, V. G., and Messer, W. E., United States Rubber Co., private communication, Oct. 11, 1946; also private communication to the Reconstruction Finance Corporation, Office of Synthetic Rubber.
[2] Schmidt and Kelsey, *Ind. Eng. Chem.* **43**, 406 (1951).
[3] Maron, S. H., and Ulevitch, I. N., private communication to the Reconstruction Finance Corporation, Office of Synthetic Rubber.
[4] Svedberg and Pedersen, "The Ultracentrifuge", Oxford University Press, London, **1940**, p. 67.
[5] Schramm and Scripture, *J. Am. Ceram. Soc.* **8**, 243 (1925).
[6] Brown, *J. Phys. Chem.* **48**, 246 (1944).
[7] Norton and Speil, *J. Am. Ceram. Soc.* **21**, 89 (1938).
[8] Svedberg and Nichols, *J. Am. Chem. Soc.* **45**, 2910 (1923).
[9] *India Rubber World* **125**, 329 (1951).
[10] Brown, W. E., paper presented at the meeting of the Electron Microscope Society of America, Pittsburgh, Penna., Dec. 7, 1946.
[11] *India Rubber World* **124**, 200 (1951).
[12] *India Rubber World* **124**, 446 (1951).
[13] *India Rubber World* **118**, 245 (1948).
[14] *India Rubber World* **122**, 71 (1950).
[15] Smith, Werner, Westerhoff, and Howland, *Ind. Eng. Chem.* **43**, 212 (1951).

RUBBER HYDROCARBON IN FRESHLY TAPPED LATEX *

G. F. BLOOMFIELD

BRITISH RUBBER PRODUCERS' RESEARCH ASSOCIATION,
WELWYN GARDEN CITY, HERTFORDSHIRE, ENGLAND

INTRODUCTION

This paper summarizes the results of investigations carried out in Malaya during the period 1948–1951, with the object of characterizing the rubber hydrocarbon in fresh Hevea latex. The main questions then requiring answer were:

(1) whether rubber is already present in high-polymer form in the tree; if so, is it a mixture of polymer homologs or of narrow molecular weight distribution?
(2) Does rubber undergo any substantial change after leaving the tree?
(3) Do trees produce rubber of reasonable uniformity from one tapping to another?
(4) Is there combined oxygen in fresh rubber?
(5) Can the plasticity of rubber, or the modulus of its vulcanizate, be correlated with the molecular weight or molecular-weight distribution of the rubber?

Characterization of rubber in the consuming territories has always been handicapped by the lack of solubility of a major portion of the material. Kemp and Peters[1], for example, showed that only a small proportion of rubber prepared by coagulation of ammonia-preserved latex could be brought into solution in hydrocarbon solvents. Nor has it been found possible in this country quantitatively to extract into solution the rubber of ammoniated latex by treatment with a solvent.

Two relatively simple techniques developed in Malaya have greatly simplified the problem of characterization of the rubber hydrocarbon. First, A. I. McMullen developed an apparatus and technique for obtaining latex from the tree in a nitrogen-atmosphere in darkened vessels, and, if desired, under sterile conditions. The procedure adopted has already been described[2]. Second, it was found that if fresh latex was shaken with a considerable volume of benzene, a homogeneous solution was obtained within a few minutes. The water of the latex was dispersed in the solution, but was readily removed by partial concentration at room temperature (30° C) under reduced pressure.

Alternatively, by use of a vistex solvent system of hydrophilic and hydrophobic liquids, the rubber and water could be brought into a homogeneous four-component system. Since the highly polar component may influence the shape and, hence, the intrinsic viscosity of rubber molecules in solution, it seemed preferable to use only nonpolar solvents and to remove the water as described above. Vistex techniques were, however, very suitable for obtaining solutions for fractionation.

* Reprinted from the *Proceedings of the Institution of the Rubber Industry*, Vol. 1, No. 3, pages 85-92, June 1954.

The reduced inherent viscosity of the benzene solution of the rubber hydrocarbon was evaluated and found to be substantially independent of concentration over the range 0.01–0.05 g. per 100 cc. and, consequently, approximately equal to the intrinsic viscosity. The intrinsic viscosity value so obtained has been designated Latex Solution Viscosity (L.S.V.). These solutions contained not only the rubber, but also all of the benzene-soluble nonrubbers, some of which were of a highly polar character and had the effect of lowering solution viscosity. Hence rubbers precipitated from these solutions had intrinsic viscosity relatively greater than could be accounted for simply by a dilution effect of the nonrubbers.

That this increase of intrinsic viscosity was not due to any permanent change in the rubber brought about by precipitation and drying was demonstrated by

TABLE I

PRECIPITATION OF RUBBER FROM LATEX SOLUTIONS BY A STANDARD PROCEDURE (ADDITION OF AN EQUAL VOLUME OF 30 PER CENT BENZENE IN METHANOL)

Intrinsic viscosity of			
Latex solution	Redissolved precipitated rubber	Ratio of intrinsic viscosities	Percentage rubber precipitated*
4.8	7.12	1.5	69
5.4	7.57	1.4	75
4.9	6.71	1.4	79
6.3	8.47	1.3	85
5.6	7.37	1.3	87
7.2	9.18	1.25	87
5.0	6.50	1.3	87.5

* Expressed as percentage of total solids in solution.

adding back to a solution of the precipitated rubber that portion of the nonrubbers eliminated on precipitation, whereby the original intrinsic viscosity was restored.

It was also shown that no increase in intrinsic viscosity resulted from coagulation of the rubber and its conversion to crepe or smoked sheet. On the contrary, such processing tended to be somewhat degradative and so to reduce the intrinsic viscosity.

ORDER OF MAGNITUDE OF INTRINSIC VISCOSITY

The intrinsic viscosity is of a generally high order compared with values observed in the rubber consuming territories. It was observed that any given tree not only shows little variation of intrinsic viscosity between successive tappings, but, more important, shows the absence of any trends throughout the year, as might be expected at refoliation or wet periods.

TABLE II

FRACTIONS FROM SMOKED SHEET AFTER REMOVING GEL

Component	Percentage in rubber	Intrinsic viscosity	Nitrogen content (per cent)
Gel	30–40	—	1–2
First fraction (pptd.)	15–25	10–11	0.2
Rest	40–50	5–7	0.1

TABLE III

FRACTIONATION OF A VISTEX SOLUTION OF WHITE FRACTION OF LATEX IN BENZENE–ISOPROPANOL

Consecutive precipitation temperatures	Yield (per cent of total rubber)	Intrinsic viscosity	Nitrogen content (per cent)
32.5°	14.2	Insoluble	2.17
31.3°	26.6	11.52	0.33
30.0°	15.0	10.48	0.10
28.5°	7.4	7.92	0.07
27.0°	3.3	6.62	0.03
25.0°	2.5	4.14	0.01
10°	15.0	2.38	0.003
Residue	16.2	Degraded and contaminated with non-rubbers	

FRACTIONATION

A high order of magnitude of intrinsic viscosity was again observed in fractionation experiments, whether carried out on fresh smoked sheet after removing gel or on solutions obtained direct from latex.

LOW FRACTIONS

The last fractions in the above fractionation (Table 3) contained considerable nonrubber relative to the amount of rubber present. It was also possible that they contained cumulative degradation products. In order to check on the latter possibility, low fractions were allowed to diffuse out of vacuum-dried

TABLE IV

INTRINSIC VISCOSITIES AND OSMOTIC MOLECULAR WEIGHTS OF SOME HEVEA HYDROCARBON FRACTIONS

Intrinsic viscosity $[\eta]$	Osmotic M.W. molecular weight	Viscosity molecular weight calculated from $[\eta] = 5.02 \times 10^{-4} M^{0.667}$
9.7	$>2 \times 10^6$	2.5×10^6
7.9	$>2 \times 10^6$	1.8×10^6
5.96	1.1×10^6	1.2×10^6
5.72		
3.80	0.8×10^6	0.6×10^6
3.73		
2.86	0.25 to 0.35×10^6	0.4×10^6

freshly-coagulated rubber by immersing it in solvent-nonslovent mixtures too rich in nonsolvent to be capable of dissolving the total rubber. In this way it was shown beyond doubt that low-molecular fractions were present in the rubber.

In all low fractions with intrinsic viscosity below 1.0, positive confirmation of the presence of combined oxygen was obtained, the amount rising to as much as 1 per cent of oxygen in fractions with intrinsic viscosity low 0.5.

OSMOTIC CONFIRMATION OF MOLECULAR WEIGHT

Confirmation of the high order of molecular weight indicated by the intrinsic viscosity followed from osmotic measurements in a set of small Zimm-Myerson osmometers.

These osmometers were not entirely suitable for molecular weights above a million, and only a restricted range of fractions, not very representative of the major proportion of the rubber, were examined. Subsequently, one of the high intrinsic viscosity fractions has been examined in a Fuoss-Mead osmometer, and a molecular weight in the region of five million has been found.

THE GEL COMPONENT IN FRESH RUBBER

Although homogeneous solutions were obtained when latex was shaken with benzene, it was found that extraction with purified petroleum ether under conditions avoiding any agitation (even that due to convection currents) left a finely divided gel component suspended in the solvent. This is believed to be microgel, i.e., gel confined to particles of colloidal dimensions. On gentle agitation it dispersed into a solution which was of rather lower intrinsic viscosity than the extracted soluble component. This behavior is quite different from that of the insoluble macrogel obtained on extracting bulk rubber.

Although benzene solutions of the rubber hydrocarbon of fresh latex show no visible gel and are filterable, the presence of microgel is revealed by light

TABLE V

INTRINSIC VISCOSITIES, MOONEY VISCOSITIES, AND GEL CONTENTS

Tree no.	Intrinsic viscosity of: Latex solution	Intrinsic viscosity of: Smoked sheet	Mooney viscosity of smoked sheet	Gel content: Dried latex*	Gel content: Smoked sheet**
1	4.95	4.85	47	21	51
2	5.15	5.59	110	59	70
14	5.25	5.50	50	27	60
3	4.8	—	45	—	—
15	5.7	6.16	110	71	88
16	6.2	—	72	—	—
17	7.6	7.32	115	67	85

* Petroleum-insoluble gel.
** Gel insoluble in a mixture (80/20 by volume) of benzene-methanol at 30° C.

scattering, and it is undoubtedly the microgel separated in the first fractions of a fractionation procedure such as that illustrated by Table III which is responsible for the subsequent insolubility of such fractions after removal of solvent. Comparable with the insolubilization of these fractions is the compacting of microgel into macrogel during coagulation and sheeting of rubber, but the tendency for gel formation by the random cross-linking of linear molecules (more especially those of higher molecular weight) must also be admitted as a source of macrogel.

THE RELATIONSHIP BETWEEN INTRINSIC VISCOSITY AND PLASTICITY

If a given rubber is progressively broken down, the intrinsic viscosity and Mooney viscosity are closely correlated. Between different rubbers, however, the intrinsic viscosity does not give a wholly reliable guide to the Mooney viscosity especially where there are large differences in the gel-content (Table V).

Figure 1 shows remarkable osmotic differences between the first three rubbers in Table V, which are, nominally, of the same intrinsic viscosity.

On storage in a dry atmosphere rubbers generally tend to harden[3]. This change is associated with an increase in gel content but with no very marked change in the intrinsic viscosity of the soluble component.

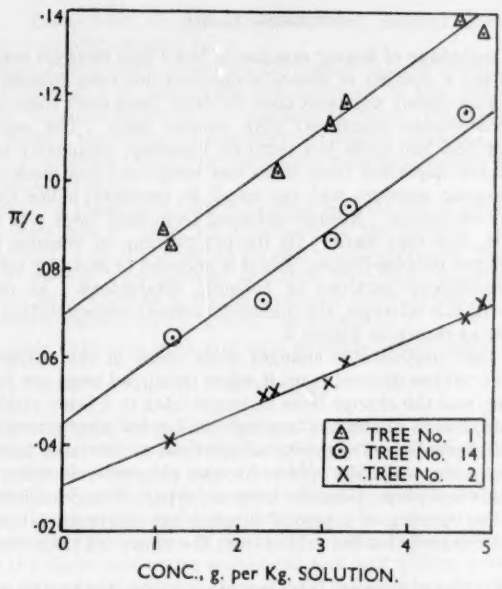


FIG. 1.—Osmotic data for rubbers from different trees giving similar L.S.V. 5.0 ± 0.2.

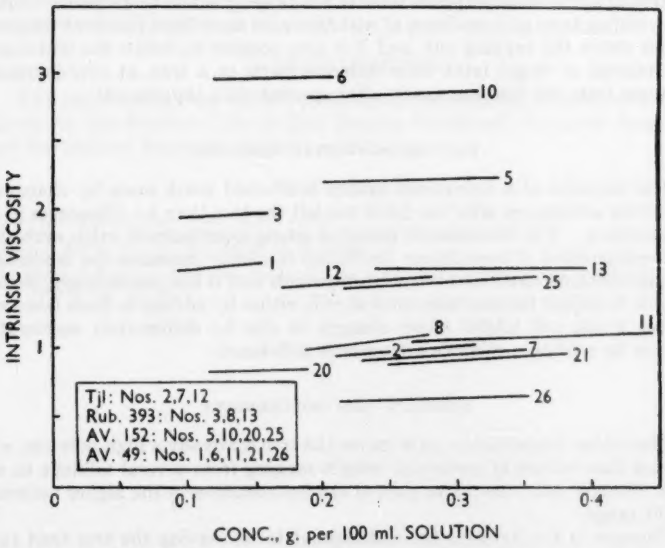


FIG. 2.—Change of inherent viscosity of microgel solutions with concentration.

MICROGEL LATEX

When the technique of taking samples of latex into benzene was applied to trees representing a number of clones which had not been tapped for several years, it was immediately apparent that the latex from such trees had unusual solubility characteristics compared with normal latex. The solutions were somewhat hazy and had quite low intrinsic viscosity, frequently in the range 0.5 to 1.0; rubber deposited from them was tough and incapable of being redissolved. Osmotic pressure was too small to measure; hence the dispersed molecules were enormous. Rubber obtained from such latex was tough, generally insoluble, and very hard. Its limited swelling in benzene indicated a considerable degree of cross-linking, and it is believed to be a true microgel latex containing cross-linked particles of colloidal dimensions. As observed by Baker[4] with synthetic microgel, the inherent viscosity concentration curves had a positive slope as shown in Figure 2.

It follows that considerable changes must occur in the characteristics of latex and of the rubber derived from it when untapped trees are brought into regular tapping, and the change from microgel latex to a latex yielding normal rubber was complete in about ten tappings (half spiral alternate daily). During this period, the inherent viscosity of solutions of the latex increased from about 1 to 4 or more, while the rubber became progressively softer, providing an example of inverse proportionality between plasticity and intrinsic viscosity.

Similarly, the opening of a second tapping cut above an existing tapping panel provided markedly harder rubber from the upper cut than from the lower one.

The identification of microgel latex in a given part of the tree thus shows that latex in that part of the tree has not been withdrawn by tapping, and enables the area of a tree which supplies latex to the tapping cut to be defined. Certain high yielding trees give evidence of withdrawal of latex from points as remote as 30 feet above the tapping cut, and it is also possible to follow the withdrawal and renewal of virgin latex from different parts of a tree, at ever-increasing distances from the tapping panel, after opening up a tapping cut.

FACTORS AFFECTING MODULUS

The modulus of a vulcanized rubber is affected much more by changes in nonrubber substances after the latex has left the tree than by differences in the hydrocarbon. The liberation of traces of nitrogenous bases or other activators by decomposition of nonrubbers (lecithins) markedly increases the modulus of mercaptobenzothiazole-accelerated compounds and it has, accordingly, become possible to adjust the modulus level at will, either by adding to fresh latex substances which will inhibit these changes or else by deliberately accelerating them or by adding a suitable nitrogenous substance.

SUMMARY AND CONCLUSIONS

The rubber hydrocarbon as it leaves the tree is already a high polymer, with a broad distribution of molecular weight ranging from several millions to well below 100,000, with the major part of the hydrocarbon in the higher molecular weight range.

Changes in the hydrocarbon subsequent to its leaving the tree tend to be degradative, but may also involve cross-linking reactions, leading to changes of

plasticity. These latter changes are particularly marked on storage, either of dry rubber or of ammoniated latex.

A microgel component present in the freshly tapped hydrocarbon is of considerable importance in influencing the hardness of raw rubber, but greatly complicates the interpretation of viscometric data. Plasticity and intrinsic viscosity cannot, therefore, be generally correlated, although the plasticity is undoubtedly influenced by the spread of the molecular-weight distribution into lower molecular regions.

It is believed that the presence of high proportions of microgel in latex of untapped trees and of branches remote from the tapping panel of trees in regular tapping, and the presence of combined oxygen in the low molecular fractions of rubber hydrocarbon obtained from both normal and microgel latexes, may be of interest in connection with biosynthesis and metabolism of the rubber hydrocarbon of the Hevea brasiliensis.

A full account of this work has been published elsewhere[5].

SUMMARY

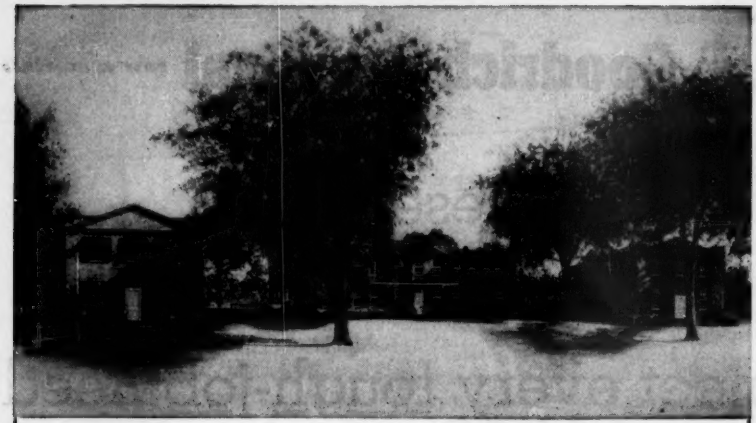
Investigations carried out in Malaya have shown that rubber hydrocarbon in fresh latex is already a high molecular material but of considerable heterogeneity. Latex is separable into non-rubber constituents and rubber hydrocarbon, which is itself separable into microgel, soluble fractions covering a wide range of molecular weight, and low-molecular oxygenated fractions. The molecular weight distribution of the soluble hydrocarbon material is weighted heavily in the higher molecular weight range of half million to five million, with an average around one million. Coagulated rubber contains macrogel in addition to the microgel component of the latex. The microgel component of latex hydrocarbon has been used as a "marker" to indicate from what regions of a tree rubber is withdrawn on tapping.

ACKNOWLEDGMENT

This paper formed part of the program of fundamental research undertaken jointly by the Boards of the British Rubber Producers' Research Association and the Rubber Research Institute of Malaya.

REFERENCES

[1] Kemp and Peters, *J. Phys. Chem.* **43**, 923 (1939).
[2] McMullen, *Nature* **164**, 715 (1949); *J. Rubber Research* **13**, 128 (1951.
[3] Wood, *J. Rubber Research Inst. Malaya* **14**, 20 (1952).
[4] Baker, *Ind. Eng. Chem.* **41**, 511 (1949).
[5] Bloomfield, *J. Rubber Research Inst. Malaya* **13**, Communications nos. 271–273; RUBBER CHEM. & TECHNOL. **24**, 737 (1951).



THE VANDERBILT LABORATORY

. . . Located in East Norwalk, Connecticut. Maintained as a Development and Technical Service Center in the Interest of Our Customers and Their Efficient Use of Vanderbilt Materials for Dry Rubber, Latex, and Plastics Compounding.

Products of Vanderbilt Research it Will Pay You to Investigate . . .

BISMATE in rubber or GR-S- rubber blends

CUMATE in GR-S

TELLURAC in Butyl

. . . Practical and powerful dithiocarbamate ultra accelerators for faster curing compounds.

R. T. VANDERBILT CO. INC.

230 Park Avenue, New York 17, N. Y.

News about

B. F. Goodrich Chemical *raw materials*

These 4 "Cold" Hycar Rubbers meet every tough-job need

THESE "cold" polymerized types of Hycar rubber have a host of applications, especially where toughest conditions must be met. Each offers specific advantages, that can help you improve or develop more saleable products. Check over each one, and write us for helpful technical information on your specific requirements. Please write Dept. HD-4, B. F. Goodrich Chemical Company, Rose Building, Cleveland 15, Ohio. Cable address: Goodchemco. In Canada: Kitchener, Ontario.

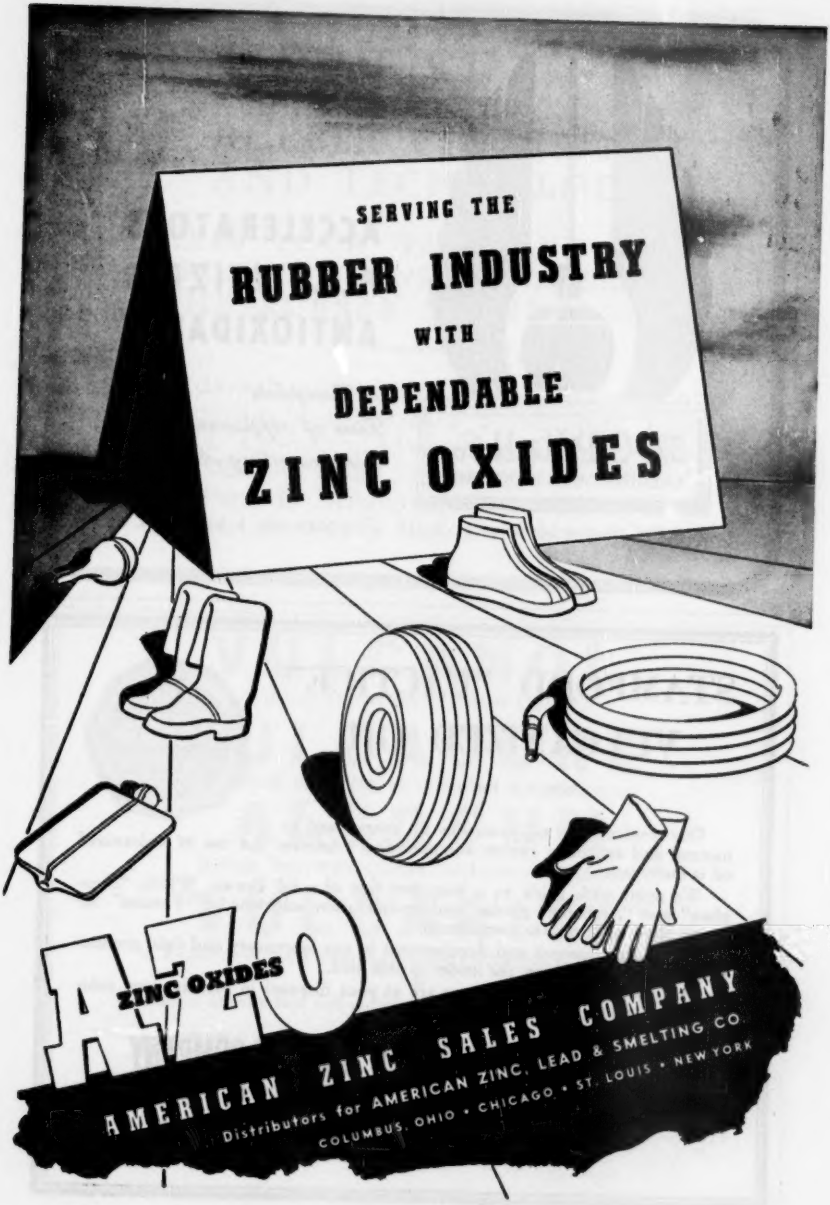
Hycar 1041	***High acrylonitrile copolymer.*** Easy processing, excellent oil and solvent resistance. Used for oil well parts, fuel cell liners, fuel hose, rolls, lathe cut gaskets, packings, "O" rings, etc.
Hycar 1042	***Medium acrylonitrile copolymer.*** Easy processing, very good oil and solvent resistance, good water resistance, excellent solubility Used for shoe soles, kitchen mats, printing rolls, "O" rings, gaskets, etc. GR-S and vinyl resin modifications, adhesives and cements.
Hycar 1043	***Medium low acrylonitrile copolymer.*** Easy processing, good oil and solvent resistance, very good low temperature properties. Used for gaskets, grommets, "O" rings, hose and other applications which require improved low temperature properties.
Hycar 1432	***Crumb form—Medium acrylonitrile copolymer.*** Directly soluble—no milling required. Used for cements and adhesives.

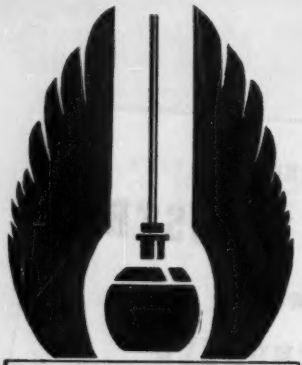
B. F. Goodrich Chemical Company

A Division of The B. F. Goodrich Company

Hycar Reg. U.S. Pat. Off. *American Rubber*

GEON polyvinyl materials • HYCAR American rubber • GOOD-RITE chemicals and plasticizers • HARMON colors


SERVING THE
RUBBER INDUSTRY
WITH
DEPENDABLE
ZINC OXIDES
AZO
ZINC OXIDES
AMERICAN ZINC SALES COMPANY
Distributors for AMERICAN ZINC, LEAD & SMELTING CO.
COLUMBUS, OHIO • CHICAGO • ST. LOUIS • NEW YORK



The C.P. Hall Co.
CHEMICAL MANUFACTURERS

ACCELERATORS
PLASTICIZERS
ANTIOXIDANTS

A Complete Line of Approved Compounding Materials

AKRON, OHIO • LOS ANGELES, CALIF. • CHICAGO, ILL. • NEWARK, N. J.

STAMFORD "FACTICE" VULCANIZED OIL

(Reg. U. S. Pat. Off.)

Our products are engineered to fill every need in natural and synthetic rubber compounding wherever the use of vulcanized oil is indicated.

We point with pride to a complete line of solid Brown, White, "Neophax" and "Amberex" grades, and hydrocarbon solutions of "Factice" for use in their appropriate compounds.

Continuing research and development in our laboratory and rigid production control has made us the leader in this field.

The services of our laboratory are at your disposal in solving your compounding problems.

THE STAMFORD RUBBER SUPPLY COMPANY
STAMFORD, CONNECTICUT

Manufacturers of "Factice" Brand Vulcanized Oil Since 1900

ADVERTISE *in*

RUBBER CHEMISTRY AND TECHNOLOGY

KEEP YOUR NAME AND YOUR PRODUCTS CONSTANTLY BEFORE THE RUBBER TECHNOLOGIST

Advertising rates and information about available locations may be obtained from E. H. Krismann, Advertising Manager, Rubber Chemistry and Technology, care of E. I. du Pont de Nemours & Company, 40 East Buchtel Ave. at S. High St., Akron 8, Ohio.

VULCANOL®
Latex Compounds of Proven Quality

VULCACURE®
AQUEOUS SUSPENSIONS OF ULTRA ACCELERATORS

ALCOGUM
Sodium Polyacrylate Latex Thickener and Stabilizer

VULCARITE®
A Series of Water Dispersions of Latex Compounding Chemicals

●

Technical information and samples forwarded promptly upon request.

ALCO OIL & CHEMICAL CORP.
TRENTON AVE. AND WILLIAM ST., PHILADELPHIA 34, PA.

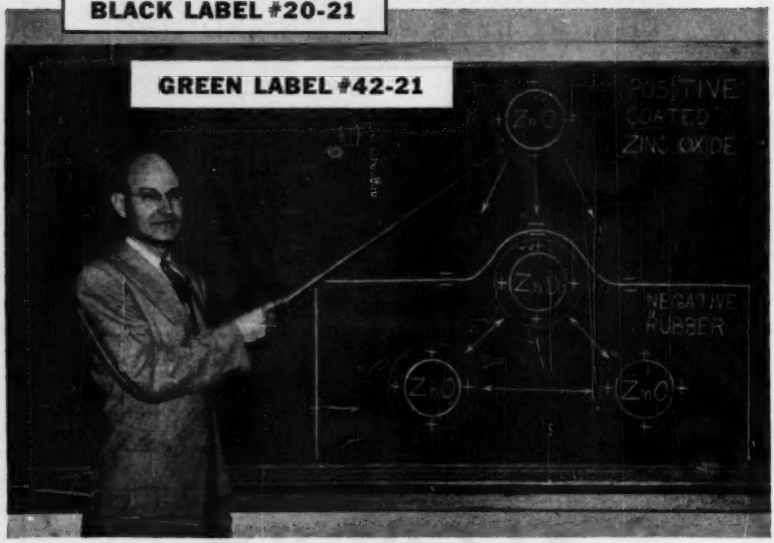
WEST COAST REPRESENTATIVE:
H. M. Royal, Inc.
Whse., 4814 Loma Vista Ave.,
Los Angeles 58, Calif.

NEW ENGLAND OFFICE
Alco Oil & Chemical Corp.
610 Industrial Trust Bldg.
111 Westminster St.,
Providence 3, R. I.

This is the main point... make a factory test with

ST. JOE *coated* ZnO

BLACK LABEL #20-21



The monomolecular film of hydrophobic, high molecular weight organic ester on St. Joe's coated zinc oxide has a more positive charge than that of rubber. Thus, the rubber has a greater affinity for St. Joe's coated zinc oxide than for an uncoated pigment with consequent reduction in incorporation time. The repelling force of the positively charged film on the zinc oxide particles themselves gives improved dispersion in less time by preventing agglomeration.

OUR 6-PAGE ILLUSTRATED FOLDER, CONTAINING DETAILED OPERATING DATA ON THE ST. JOE UNIT-LOAD METHOD IS YOURS FOR THE ASKING.

ST. JOSEPH LEAD COMPANY
250 Park Avenue, New York 17
Plant & Laboratory: Monaca (Josephtown) Pa.

Now Available **— A new English-language Text Book on Rubber**

RUBBER: Natural and Synthetic

By H. J. STERN

A Comprehensive Treatise on Production and Processing including Compounding Ingredients, Machinery and Methods for the Manufacture of various Rubber Products.

First Edition — 491 Pages — 200 Illustrations

PRICE: $12.00* Postpaid in U. S.

Second Edition of

LATEX in INDUSTRY

By ROYCE J. NOBLE, Ph.D.

912 Pages • 6 x 9 Inches • 25 Chapters
Bibliography • Author Index • Subject Index

PRICE: $15.00* Postpaid in U. S.
$16.00 Postpaid in All Other Countries

(*) Add 3% Sales Tax for Copies to New York City Addresses

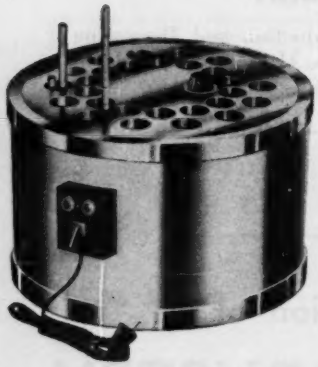
Available from

RUBBER AGE

250 West 57th St. New York 19, N. Y.

TESTED IS TRUSTED

Do you want to test compounds for deterioration at EXTREME TEMPERATURES?



Up to 450°F

MODEL LG AGEING TESTER

For Temperature Ageing Tests of elastomers —also for Oxygen Ageing Studies. Here is an insulated solid aluminum block oven, with built-in electric heating elements and temperature controls. The individual isolated compartments eliminate errors due to contamination between samples. 2 models: 28 compartments 1½" dia. for temperature ageing; also with a lesser number of larger compartments for oxygen ageing. For ASTM Test No. D865–52T.

As low as -80°C

BRITTLE POINT TESTER

With a range of +50° to −80° C, this tester—which is self-contained and readily portable —can produce extremes of temperature under which plastics and rubber shatter like glass. Conforms to ASTM Designation D746–52T.

REQUEST LITERATURE

SCOTT TESTERS, INC. 102 Blackstone St. Providence, R. I.

Scott Testers — Standard of the World

ANTIMONY SULPHIDE

Regular Grades *for* Attractive Color

Also

A special grade for obtaining colored stocks having high abrasion resistance

RARE METAL PRODUCTS CO. **ATGLEN, PENNA.**

SUPERIOR ZINC CORPORATION

121 North Broad Street **Philadelphia 7, Penna.**

Works at Bristol, Pa.

VULCANIZED VEGETABLE OILS

• RUBBER SUBSTITUTES •

THE CARTER BELL MFG. CO. SINCE CARTER BELL PRODUCTS 1903 SPRINGFIELD, NEW JERSEY

REPRESENTED BY

HARWICK STANDARD CHEMICAL CO.

Akron — Boston — Trenton — Chicago — Denver — Los Angeles

Ready Now!

MACHINERY and EQUIPMENT for RUBBER and PLASTICS

VOLUME I
PRIMARY MACHINERY AND EQUIPMENT

The only book of its kind ever offered to the Rubber and Plastics Industries and the first to be published since Pearson's "Rubber Machinery" in 1915. Compiled by Robert G. Seaman and Arthur M. Merrill, the present Editors of India RUBBER WORLD, with the cooperation of an Editorial Advisory Board of experts in their respective fields. Each chapter is preceded by an article written by recognized authorities on the equipment, its purposes for specific products, and best method of using it.

Volume I has over 800 pages of editorial content with authoritative descriptions for each machine classification: Types, Specifications, Design Features, Operation, and Applications, as well as names and addresses of the manufacturers or suppliers. More than 300 illustrations. Cloth-bound for permanence.

Send for free copy of complete prospectus.

Volume I—$15.00 Postpaid in U. S. A.
$16.00 Elsewhere

Volume II—Supplementary Machinery and Equipment, is now in preparation and will be published in the near future.

INDIA
RUBBER WORLD
386 FOURTH AVENUE NEW YORK 16, N. Y.

WHITETEX

A new white and bright pigment for rubber, synthetic rubber or plastics, especially vinyls.

BUCA

A proved pigment for compounding ALL types of natural and synthetic rubber.

CATALPO

For compounding rubber and synthetic rubber.

No. 33 CLAY

For wire and vinyl compounding.

●

For full details, write our Technical Service Dept.

SOUTHERN CLAYS, INC.

(Formerly P. W. Martin Gordon Clays, Inc.)

33 Rector Street · New York 6, N.Y.

RUBBER CHEMISTRY AND TECHNOLOGY IS SUPPORTED BY ADVERTISING FROM THESE LEADING SUPPLIERS

INDEX TO ADVERTISERS

	Page
Alco Oil and Chemical Corp.	23
American Cyanamid Company, Organic Chemicals Division	12
American Zinc Sales Company	21
Binney & Smith Company...(Opposite Table of Contents)	18
Cabot, Godfrey L., Inc.	11
Carter Bell Manufacturing Company, The	27
Du Pont Rubber Chemicals Division	32
Goodrich, B. F., Chemical Company	20
Goodyear Tire & Rubber Company, The	5
Hall, C. P., Company, The	22
Harwick Standard Chemical Company....(Inside Back Cover)	
Huber, J. M., Corporation	31
India Rubber World	28
Koppers Company, Inc. (Chemical Division)	13
Monsanto Chemical Company	7
Naugatuck Chemical Division (U. S. Rubber Company)...	15
Neville Chemical Company	14
New Jersey Zinc Company, The .....(Outside Back Cover)	
Pan-American Refining Corp., Pan American Chemicals Div.	8
Phillips Chemical Company .(Opposite Inside Front Cover)	1
Rare Metal Products Company	27
Richardson, Sid, Carbon Company	6
Rubber Age, The	25
St. Joseph Lead Company	24
Scott Testers, Inc	26
Sharples Chemicals, Inc.	3
Southern Clays, Inc.	29
Stamford Rubber Supply Company, The	22
Sun Oil Company, Sun Petroleum Products (Opposite Title Page)	16
Superior Zinc Corporation	27
Thiokol Chemical Corporation	4
Titanium Pigment Corporation	31
United Carbon Company .....(Inside Front Cover)	
Vanderbilt, R. T., Company	19
Wiley, John & Sons, Inc.	9
Witco Chemical Company	2

CARBON BLACKS

Wyex (EPC)
Easy Processing Channel Black

Arrow TX (MPC)
Medium Processing Channel Black

Essex (SRF)
Semi-Reinforcing Furnace Black

Modulex (HMF)
High Modulus Furnace Black

Aromex (HAF)
High Abrasion Furnace Black

Aromex 115 (CF)
Conductive Furnace Black

Aromex 125 (ISAF) Intermediate
Super Abrasion Furnace Black

Arovel (FEF)
Fast Extruding Furnace Black

Collocarb
80% Carbon Black + 20% Process Oil

CLAYS

Suprex Clay . . . . High Reinforcement
Paragon Clay . . . . . Easy Processing
Hi-White R . . . . . White Color

RUBBER CHEMICALS

Turgum S, Natac, Butac . . . . . Resin-Acid Softeners
Aktone . . . . . Accelerator Activator
Zeolex 23 . . . . . Reinforcing White Pigment

HUBER J. M. HUBER CORPORATION • 100 Park Ave., New York 17, New York

consult **TITANOX** *technical service department*

for assistance with your white pigmentation problems

TITANIUM PIGMENT CORPORATION
Subsidiary of NATIONAL LEAD COMPANY

TITANOX
the brightest name in pigments

Your Product Deserves

DU PONT RUBBER CHEMICALS

dependable in performance . . . uniform in quality

ACCELERATORS

Accelerator 89
Accelerator 552
Accelerator 808*
Accelerator 833*
Butyl Accelerator 21
DOTG
2—MT
MBT
MBTS
NA—22
Permalux*
Polyac*
Tepidone*
Tetrone*A
Thionex*
Thionex*Grains
Thiuram E
Thiuram M
Thiuram M Grains
Zenite*
Zenite*A
Zenite*Special

ANTIOXIDANTS

Akroflex*C
Akroflex*CD
Antox*
Neozone*A
Neozone*D
Permalux*
Thermoflex*A

AQUAREXES

Aquarex*L
Aquarex*D
Aquarex*G
Aquarex*MDL
Aquarex*ME
Aquarex*NS
Aquarex*SMO
Aquarex*WAQ

BLOWING AGENTS

Unicel
Unicel ND
Unicel S

COLORS

RUBBER DISPERSED COLORS	WATER DISPERSIBLE COLORS
Rubber Red PBD	Rubber Red PBL
Rubber Red 2BD	Rubber Red 2BL
Rubber Orange OD	Rubber Yellow GL
Rubber Yellow GD	Monastral*Rubber Blue CPL
Rubber Green FD Monastral*	Monastral*Rubber Green GSL
Rubber Green GSD Monastral*	
Rubber Blue PCD	
Rubber Blue GD	

ISOCYANATES

"HyLene"* M "HyLene" M-50
Organic Isocyanate

PEPTIZING AGENTS

RPA No. 2
RPA No. 3
RPA No. 3 Concentrated
RPA No. 5
RPA No. 6

RECLAIMING CHEMICALS

RPA No. 3
RR-10

SPECIAL PURPOSE CHEMICALS

Barak*—Accelerator activator
Copper Inhibitor X-872-L—Inhibits catalytic action of copper on elastomers.
ELA—Elastomer lubricating agent
Heliozone*—Sun checking inhibitor
NBC—Inhibits weather cracking of GR-S
Retarder W—Accelerator retarder

*REG. U. S. PAT. OFF.

DU PONT

BETTER THINGS FOR BETTER LIVING . . . THROUGH CHEMISTRY
E. I. DU PONT DE NEMOURS & CO. (INC.) · RUBBER CHEMICALS DIVISION
WILMINGTON, DELAWARE

Material for ALL RUBBER and PLASTIC COMPOUNDING

PRECISION Uniformity

You can depend upon the *Precision* character of Harwick Standard Chemicals regardless of the quantity requirement . . . Here is dependable assurance of uniformity in any type compounding material for rubber and plastics to give *certainty* in product development and production runs.

Our services are offered in co-operative research toward the application of any compounding material in our line to your production problems.

HARWICK STANDARD CHEMICAL CO.

AKRON 5, OHIO

BRANCHES: BOSTON, TRENTON, CHICAGO, LOS ANGELES

You can formulate *FASTER... BETTER* with

HORSE HEAD® ZINC OXIDES

FORMULATE FASTER!

... Because the Horse Head line comprises the most complete family of Zinc Oxides for rubber:

1. It is the only line having such a wide range of particle sizes, surface conditions and chemical compositions.
2. Its *conventional* types cover the range of American and French Process oxides.
3. Its *exclusive* types include the well-known Kadox and Protox brands.

That means you need not waste time adapting a single Zinc Oxide to each specific compound. Instead, just choose from the Horse Head line the Zinc Oxides that best meet your needs.

FORMULATE BETTER!

... Because you need to compromise less when you choose from the wide variety of Horse Head Zinc Oxides.

... Because the Horse Head brands can improve the properties of your compounds.

Year after year, for nearly a century, more rubber manufacturers have used more tons of Horse Head Zinc Oxides than of any other brands.

THE NEW JERSEY ZINC COMPANY

Founded 1848

160 Front Street, New York 38, N. Y.